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Section IV

ORGANIC MOLECULAR FUNCTIONAL GROUPS AND MOLECULES

5 Organic molecules comprising an arbitrary number of atoms can be solved using the similar principles and procedures as those used to solve alkanes of arbitrary length. Alkanes can be considered to be comprised of the functional groups of CH_3 , CH_2 , and C-C. These groups with the corresponding geometrical parameters and energies can be added as a linear sum to give the solution of any straight chain alkane as shown in the Continuous-Chain Alkanes 10 section. Similarly, the geometrical parameters and energies of all functional groups such as alkanes, branched alkanes, alkenes, branched alkenes, alkynes, alkyl fluorides, alkyl chlorides, alkyl bromides, alkyl iodides, alkene halides, primary alcohols, secondary alcohols, tertiary alcohols, ethers, primary amines, secondary amines, tertiary amines, aldehydes, ketones, carboxylic acids, carboxylic esters, amides, N-alkyl amides, N,N-dialkyl amides, 15 urea, acid halides, acid anhydrides, nitriles, thiols, sulfides, disulfides, sulfoxides, sulfoxes, sulfites, sulfates, nitro alkanes, nitrites, nitrates, conjugated polyenes, aromatics, heterocyclic aromatics, substituted aromatics, and others can be solved. The functional-group solutions can be made into a linear superposition and sum, respectively, to give the solution of any organic molecule. The solutions of the functional groups can be conveniently obtained by 20 using generalized forms of the geometrical and energy equations. The equations and sections that are referenced by not contained in this text refer to those sections and equations of the book by R. L. Mills entitled, "The Grand Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834; posted at 25 http://www.blacklightpower.com/bookdownload.shtml which is incorporated in its entirety by reference.

Consider the case wherein at least two atomic orbital hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum, and the sharing of electrons between two or more such orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. The force generalized constant k' of a

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 H_2 -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\varepsilon_0} \tag{15.1}$$

where C_1 is the fraction of the H_2 -type ellipsoidal MO basis function of a chemical bond of the molecule or molecular ion which is 0.75 (Eq. (13.59)) in the case of H bonding to a 5 central atom and 0.5 (Eq. (14.152)) otherwise, and C_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of the chemical bond. From Eqs. (13.58-13.63), the distance from the origin of the MO to each focus c' is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}}$$
 (15.2)

10 The internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.3}$$

The length of the semiminor axis of the prolate spheroidal MO b = c is given by

$$b = \sqrt{a^2 - c'^2} \tag{15.4}$$

And, the eccentricity, e, is

$$15 e = \frac{c'}{a} (15.5)$$

From Eqs. (11.207-11.212), the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_e = n_1 c_1 c_2 \frac{-2e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
(15.6)

The potential energy of the two nuclei is

$$V_{p} = n_{1} \frac{e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2} - b^{2}}}$$
 (15.7)

The kinetic energy of the electrons is

$$T = n_1 c_1 c_2 \frac{\hbar^2}{2m_2 a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
(15.8)

And, the energy, V_m , of the magnetic force between the electrons is

$$V_{m} = n_{1}c_{1}c_{2}\frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}}\ln\frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}}$$
(15.9)

The total energy of the H_2 -type prolate spheroidal MO, E_T (H_2MO), is given by the sum of the energy terms:

$$E_{T}(H_{2}MO) = V_{e} + T + V_{m} + V_{n}$$
(15.10)

$$E_{T}(\mu_{2}MO) = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2} - b^{2}}} \left[c_{1}c_{2}\left(2 - \frac{a_{0}}{a}\right) \ln\frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} - 1 \right]$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}c'} \left[c_{1}c_{2}\left(2 - \frac{a_{0}}{a}\right) \ln\frac{a + c'}{a - c'} - 1 \right]$$
(15.11)

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where n_1 is the number of equivalent bonds of the MO and applies in the case of functional groups. In the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by c_{BO} , the bond-order factor. It is 1 for a single bond, 4 for an independent double bond as in the case of the CO_2 and NO_2 molecules, and 9 for an 10 independent triplet bond. Then, the kinetic energy term is multiplied by c'_{BO} which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond. c_1 is the fraction of the H_2 -type ellipsoidal MO basis function of an MO which is 0.75 (Eqs. (13.67-13.73)) in the case of Hbonding to an unhybridized central atom and 1 otherwise, and \boldsymbol{c}_2 is the factor that results in an equipotential energy match of the participating the MO and the at least two atomic orbitals 15 of the chemical bond. Specifically, to meet the equipotential condition and energy matching conditions for the union of the H_2 -type-ellipsoidal-MO and the HOs or AOs of the bonding atoms, the factor c_2 of a H_2 -type ellipsoidal MO may given by (i) one, (ii) the ratio of the Coulombic or valence energy of the AO or HO of at least one atom of the bond and $13.605804 \, eV$, the Coulombic energy between the electron and proton of H, (iii) the ratio of 20 the valence energy of the AO or HO of one atom and the Coulombic energy of another, (iv) the ratio of the valence energies of the AOs or HOs of two atoms, (v) the ratio of two c_2 factors corresponding to any of cases (ii)-(iv), and (vi) the product of two different c_2 factors corresponding to any of the cases (i)-(v). Specific examples of the factor c_2 of a H_2 -type ellipsoidal MO given in previous sections are

0.936127, the ratio of the ionization energy of N 14.53414 eV and 13.605804 eV, the Coulombic energy between the electron and proton of H;

0.91771, the ratio of 14.82575
$$eV$$
, $-E_{Coulomb}(C,2sp^3)$, and 13.605804 eV ; 0.87495, the ratio of 15.55033 eV , $-E_{Coulomb}(C_{ethane},2sp^3)$, and 13.605804 eV ; 0.85252, the ratio of 15.95955 eV , $-E_{Coulomb}(C_{ethylene},2sp^3)$, and 13.605804 eV ; 0.85252, the ratio of 15.95955 eV , $-E_{Coulomb}(C_{benzene},2sp^3)$, and 13.605804 eV ; and 0.86359, the ratio of 15.55033 eV , $-E_{Coulomb}(C_{alkane},2sp^3)$, and 13.605804 eV .

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In the generalization of the hybridization of at least two atomic-orbital shells to form a shell of hybrid orbitals, the hybridized shell comprises a linear combination of the electrons of the atomic-orbital shells. The radius of the hybridized shell is calculated from the total Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and that the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons. The total energy $E_T(atom, msp^3)$ (m is the integer of the valence shell) of the AO electrons and the hybridized shell is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least one AO shell.

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$$E_T(atom, msp^3) = -\sum_{m=1}^{n} IP_m$$
 (15.12)

where IP_m is the *m*th ionization energy (positive) of the atom. The radius r_{msp^3} of the hybridized shell is given by:

$$r_{msp^3} = \sum_{q=Z-n}^{Z-1} \frac{-(Z-q)e^2}{8\pi\varepsilon_0 E_T \left(atom, msp^3\right)}$$
(15.13)

Then, the Coulombic energy $E_{Coulomb}$ (atom, msp^3) of the outer electron of the atom msp^3 20 shell is given by

$$E_{Coulomb}\left(atom, msp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}}$$
(15.14)

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) at the initial radius r of the AO electron:

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$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m^2 r^3} = \frac{8\pi\mu_0 \mu_B^2}{r^3}$$
 (15.15)

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Then, the energy $E(atom, msp^3)$ of the outer electron of the $atom msp^3$ shell is given by the sum of $E_{Coulomb}(atom, msp^3)$ and E(magnetic):

$$E(atom, msp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}r^{3}}$$
(15.16)

Consider next that the at least two atomic orbitals hybridize as a linear combination of 5 electrons at the same energy in order to achieve a bond at an energy minimum with another atomic orbital or hybridized orbital. As a further generalization of the basis of the stability of the MO, the sharing of electrons between two or more such hybridized orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. In this case, the total energy of the 10 hybridized orbitals is given by the sum of $E(atom, msp^3)$ and the next energies of successive ions of the atom over the n electrons comprising the total electrons of the at least two initial AO shells. Here, $E(atom, msp^3)$ is the sum of the first ionization energy of the atom and the hybridization energy. An example of $E(atom, msp^3)$ for $E(C, 2sp^3)$ is given in Eq. (14.503) where the sum of the negative of the first ionization energy of C, $-11.27671 \, eV$, plus the $C2sp^3$ shell given by Eq. 15 hybridization energy to form the $E(C,2sp^3) = -14.63489 \ eV$.

Thus, the sharing of electrons between two $atom msp^3$ HOs to form an atom-atom-bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each $atom msp^3$ HO donates an excess of 25% per bond of its electron density to the atom-atom-bond MO to form an energy minimum wherein the atom-atom bond comprises one of a single, double, or triple bond. In each case, the radius of the hybridized shell is calculated from the Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons plus the hybridization energy. The total energy $E_T(mol.atom, msp^3)$ (m is the integer of the valence shell) of the HO electrons is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least one initial AO shell and the hybridization energy:

$$450$$

$$E_{T}\left(mol.atom, msp^{3}\right) = E\left(atom, msp^{3}\right) - \sum_{m=2}^{n} IP_{m}$$
(15.17)

where IP_m is the mth ionization energy (positive) of the atom and the sum of $-IP_1$ plus the hybridization energy is $E(atom, msp^3)$. Thus, the radius r_{msp^3} of the hybridized shell is given by:

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$$r_{msp^3} = \left(\sum_{q=Z-n}^{Z-1} (Z-q) - s(0.25)\right) \frac{-e^2}{8\pi\varepsilon_0 E_T \left(mol.atom, msp^3\right)}$$
 (15.18)

where s = 1, 2, 3 for a single, double, and triple bond, respectively. The Coulombic energy $E_{Coulomb}$ (mol.atom, msp³) of the outer electron of the atom msp³ shell is given by

$$E_{Coulomb}\left(mol.atom, msp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}}$$
(15.19)

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) at the initial radius r of the AO electron given by Eq. (15.15). Then, the energy $E(mol.atom, msp^3)$ of the outer electron of the $atom\ msp^3$ shell is given by the sum of $E_{Coulomb}$ $(mol.atom, msp^3)$ and E(magnetic):

$$E(mol.atom, msp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}r^{3}}$$
(15.20)

15 E_T (atom – atom, msp³), the energy change of each atom msp³ shell with the formation of the atom-atom-bond MO is given by the difference between E (mol.atom, msp³) and E (atom, msp³):

$$E_{T}\left(atom - atom, msp^{3}\right) = E\left(mol.atom, msp^{3}\right) - E\left(atom, msp^{3}\right)$$
(15.21)

As examples from prior sections, $E_{Coulomb}$ (mol.atom, msp³) is one of:

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$$E_{Coulomb}\left(C_{ethylene}, 2sp^3\right)$$
, $E_{Coulomb}\left(C_{ethane}, 2sp^3\right)$, $E_{Coulomb}\left(C_{acetylene}, 2sp^3\right)$, and $E_{Coulomb}\left(C_{alkane}, 2sp^3\right)$;

$$E_{Coulomb}$$
 (atom, msp³) is one of $E_{Coulomb}$ (C, 2sp³) and $E_{Coulomb}$ (Cl, 3sp³);

$$E(mol.atom, msp^3) is one of E(C_{ethylene}, 2sp^3), E(C_{ethane}, 2sp^3),$$

$$E(C_{acetylene}, 2sp^3)E(C_{alkane}, 2sp^3);$$

$$E(atom, msp^3)$$
 is one of and $E(C, 2sp^3)$ and $E(Cl, 3sp^3)$;

$$E_T$$
 (atom – atom, msp^3) is one of $E(C-C, 2sp^3)$, $E(C=C, 2sp^3)$, and $E(C\equiv C, 2sp^3)$;

atom msp^3 is one of $C2sp^3$, $Cl3sp^3$

 $E_T\left(atom-atom(s_1),msp^3\right)$ is $E_T\left(C-C,2sp^3\right)$ and $E_T\left(atom-atom(s_2),msp^3\right)$ is $E_T\left(C=C,2sp^3\right)$, and

$$r_{msp^3}$$
 is one of r_{C2sp^3} , $r_{ethane2sp^3}$, $r_{ethylene2sp^3}$, $r_{acetylene2sp^3}$, $r_{alkane2sp^3}$, and r_{Cl3sp^3} .

In the case of the $C2sp^3$ HO, the initial parameters (Eqs. (14.142-14.146)) are

10
$$r_{2sp^3} = \sum_{n=2}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0 \left(e148.25751 \, eV\right)} = \frac{10e^2}{8\pi\varepsilon_0 \left(e148.25751 \, eV\right)} = 0.91771a_0 \tag{15.22}$$

$$E_{Coulomb}\left(C, 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{2sp^{3}}} = \frac{-e^{2}}{8\pi\varepsilon_{0}0.91771a_{0}} = -14.82575 \ eV \tag{15.23}$$

$$E(magnetic) = \frac{2\pi\mu_0 e^2 h^2}{m_e^2 (r_3)^3} = \frac{8\pi\mu_0 \mu_B^2}{\left(0.84317a_0\right)^3} = 0.19086 \ eV$$
 (15.24)

$$E(C,2sp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{2sp^{3}}} + \frac{2\pi\mu_{0}e^{2}h^{2}}{m_{e}^{2}(r_{3})^{3}}$$

$$= -14.82575 \ eV + 0.19086 \ eV$$

$$= -14.63489 \ eV$$
(15.25)

In Eq. (15.18),

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$$\sum_{q=Z-n}^{Z-1} (Z-q) = 10$$
 (15.26)

Eqs. (14.147) and (15.17) give

$$E_T (mol.atom, msp^3) = E_T (C_{ethane}, 2sp^3) = -151.61569 \ eV$$
 (15.27)

Using Eqs. (15.18-15.28), the final values of r_{C2sp^3} , $E_{Coulomb}$ ($C2sp^3$), and $E(C2sp^3)$, and the resulting $E_T\left(C^{BO}_{-C},C2sp^3\right)$ of the MO due to charge donation from the HO to the MO where

C-C refers to the bond order of the carbon-carbon bond for different values of the parameter s are given in Table 15.1.

Table 15.1. The final values of r_{C2sp^3} , $E_{Coulomb}(C2sp^3)$, and $E(C2sp^3)$ and the resulting $E_T(C^{BO}_T, C_T, C_T)$ of the MO due to charge donation from the HO to the MO where C^{BO}_T refers to the bond order of the carbon-carbon bond.

MO Bond Order (BO)	s 1	s 2	$r_{C2sp^3}\left(a_0 ight)$ Final	$E_{Coulomb}$ $\left(C2sp^3\right)$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	$E_T \left(C - C, C2sp^3 \right)$ (eV)
I	1	0	0.87495	-15.55033	-15.35946	-0.72457
II	2	0	0.85252	-15.95955	-15.76868	-1.13379
III	3	0	0.83008	-16.39089	-16.20002	-1.56513
IV	4	0	0.80765	-16.84619	-16.65532	-2.02043

In another generalized case of the basis of forming a minimum-energy bond with the constraint that it must meet the energy matching condition for all MOs at all HOs or AOs, the energy $E(mol.atom, msp^3)$ of the outer electron of the atom msp^3 shell of each bonding atom must be the average of $E(mol.atom, msp^3)$ for two different values of s:

$$E(mol.atom, msp^3) = \frac{E(mol.atom(s_1), msp^3) + E(mol.atom(s_2), msp^3)}{2}$$
(15.28)

In this case, E_T ($atom-atom, msp^3$), the energy change of each $atom msp^3$ shell with the formation of each atom-atom-bond MO, is average for two different values of s:

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$$E_T \left(atom - atom, msp^3\right) = \frac{E_T \left(atom - atom(s_1), msp^3\right) + E_T \left(atom - atom(s_2), msp^3\right)}{2}$$
 (15.29)

Consider an aromatic molecule such as benzene given in the Benzene Molecule section. Each C = C double bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two $C2sp^3$ HOs of the participating carbon atoms. Each C - H bond of CH having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the

linear combination of 75% H_2 -type ellipsoidal MO and 25% $C2sp^3$ HO as given by Eq. (13.439). However, $E_T \left(atom-atom,msp^3\right)$ of the C-H-bond MO is given by $0.5E_T \left(C=C,2sp^3\right)$ (Eq. (14.247)) corresponding to one half of a double bond that matches the condition for a single-bond order for C-H that is lowered in energy due to the aromatic 5 character of the bond.

A further general possibility is that a minimum-energy bond is achieved with satisfaction of the potential, kinetic, and orbital energy relationships by the formation of an MO comprising an allowed multiple of a linear combination of H_2 -type ellipsoidal MOs and corresponding HOs or AOs that contribute a corresponding allowed multiple (e.g. 0.5, 0.75, 10 1) of the bond order given in Table 15.1. For example, the alkane MO given in the Continuous-Chain Alkanes section comprises a linear combination of factors of 0.5 of a single bond and 0.5 of a double bond.

Consider a first MO and its HOs comprising a linear combination of bond orders and a second MO that shares a HO with the first. In addition to the mutual HO, the second MO comprises another AO or HO having a single bond order or a mixed bond order. Then, in order for the two MOs to be energy matched, the bond order of the second MO and its HOs or its HO and AO is a linear combination of the terms corresponding to the bond order of the mutual HO and the bond order of the independent HO or AO. Then, in general, E_T ($atom-atom,msp^3$), the energy change of each $atom\ msp^3$ shell with the formation of each atom-atom-bond MO, is a weighted linear sum for different values of s that matches the energy of the bonded MOs, HOs, and AOs:

$$E_{T}\left(atom - atom, msp^{3}\right) = \sum_{n=1}^{N} c_{s_{n}} E_{T}\left(atom - atom\left(s_{n}\right), msp^{3}\right)$$
 (15.30)

where c_{s_n} is the multiple of the BO of s_n . The radius r_{msp^3} of the atom msp^3 shell of each bonding atom is given by the Coulombic energy using the initial energy $E_{Coulomb}$ (atom, msp^3) and E_T (atom – atom, msp^3), the energy change of each atom msp^3 shell with the formation of each atom-atom-bond MO:

$$r_{msp^{3}} = \frac{-e^{2}}{8\pi\varepsilon_{0}a_{0}\left(E_{Coulonb}\left(atom, msp^{3}\right) + E_{T}\left(atom - atom, msp^{3}\right)\right)}$$
(15.31)

where $E_{Coulomb}(C2sp^3) = -14.825751 \, eV$. The Coulombic energy $E_{Coulomb}(mol.atom, msp^3)$ of the outer electron of the $atom \, msp^3$ shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy $E(mol.atom, msp^3)$ of the outer electron of the $atom \, msp^3$ shell is given by the sum of $E_{Coulomb}(mol.atom, msp^3)$ and E(magnetic) (Eq. (15.20)). $E_T(atom-atom, msp^3)$, the energy change of each $atom \, msp^3$ shell with the formation of the atom-atom-bond MO is given by the difference between $E(mol.atom, msp^3)$ and $E(atom, msp^3)$ given by Eq. (15.21). Using Eq. (15.23) for $E_{Coulomb}(C, 2sp^3)$ in Eq. (15.31), the single bond order energies given by Eqs. (15.18-15.27) and shown in Table 15.1, and the linear combination energies (Eqs. (15.28-15.30)), the parameters of linear combinations of bond orders and linear combinations of mixed bond orders are given in Table 15.2.

15 Table 15.2. The final values of r_{C2sp^3} , $E_{Coulomb}\left(C2sp^3\right)$, and $E\left(C2sp^3\right)$ and the resulting $E_T\left(C^{BO}_{-}C,C2sp^3\right)$ of the MO comprising a linear combination of H_2 -type ellipsoidal MOs and corresponding HOs of single or mixed bond order where c_{s_n} is the multiple of the bond order parameter $E_T\left(atom-atom(s_n),msp^3\right)$ given in Table 15.1.

Table 15.1 455

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MO Bond	<i>s</i> 1	\mathcal{C}_{s_1}	<i>s</i> 2	C_{s_2}	<i>s</i> 3	C_{s_3}	$r_{C2sp^3}\left(a_0\right)$	$E_{Coulomb} \left(C2sp^3 \right)$ (eV)	$E\left(C2sp^3\right)$	$E_T \left(C - C, C2sp^3 \right)$
Order (BO)							Final	Final	(eV) Final	(eV)
1/2I	1	0.5	0	0	0	0	0.89582	-15.18804	-14.99717	-0.36228
1/2II	2	0.5	0	0	0	0	0.88392	-15.39265	-15.20178	-0.56689
I +	1	0.5	2	0.2	0	0	0.87941	-15.47149	-15.28062	-0.64573
1/2II				5						
1/2II	2	0.2	1	0.2	2	0.2	0.87363	-15.57379	-15.38293	-0.74804
+ (I +		5		5		5				
II)										
3/4II	2	0.7	0	0	0	0	0.86793	-15.67610	-15.48523	-0.85034
		5								
I + II	1	0.5	2	0.5	0	0	0.86359	-15.75493	-15.56407	-0.92918
I +	. 1	0.5	3	0.5	0	0	0.85193	-15.97060	-15.77974	-1.14485
III								•		
I +	1	0.5	4	0.5	0	0	0.83995	-16.19826	-16.00739	-1.37250
IV										
II+	2	0.5	3	0.5	0	0	0.84115	-16.17521	-15.98435	-1.34946
III										
II +	2	0.5	4	0.5	0	0	0.82948	-16.40286	-16.21200	-1.57711
IV										
III +	3	0.5	4	0.5	0	0	0.81871	-16.61853	-16.42767	-1.79278
IV ·										
IV +	4	0.5	4	0.5	0	0	0.80765	-16.84619	-16.65532	-2.02043
IV										

Consider next the radius of the AO or HO due to the contribution of charge to more than one bond. The energy contribution due to the charge donation at each atom such as 5 carbon superimposes linearly. In general, the radius r_{mol2sp^3} of the $C2sp^3$ HO of a carbon atom of a given molecule is calculated using Eq. (14.514) by considering $\sum E_{T_{mol}} (MO, 2sp^3)$, the total energy donation to each bond with which it participates in bonding. The general equation for the radius is given by

$$r_{mol2sp^{3}} = \frac{-e^{2}}{8\pi\varepsilon_{0} \left(E_{Coulomb} \left(C, 2sp^{3}\right) + \sum E_{T_{mol}} \left(MO, 2sp^{3}\right)\right)}$$

$$= \frac{e^{2}}{8\pi\varepsilon_{0} \left(e14.825751 \ eV + \sum \left|E_{T_{mol}} \left(MO, 2sp^{3}\right)\right|\right)}$$
(15.32)

The Coulombic energy $E_{Coulomb}$ (mol.atom, msp³) of the outer electron of the atom msp³ shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy $E(mol.atom, msp^3)$ of the outer electron of the atom msp^3 shell is given by the sum of $E_{Coulomb}$ (mol.atom, msp³) and E(magnetic) (Eq. (15.20)).

For example, the $C2sp^3$ HO of each methyl group of an alkane contributes $10 -0.92918 \, eV$ (Eq. (14.513)) to the corresponding single C-C bond; thus, the corresponding $C2sp^3$ HO radius is given by Eq. (14.514). The $C2sp^3$ HO of each methylene group of C_nH_{2n+2} contributes $-0.92918 \, eV$ to each of the two corresponding C-C bond MOs. Thus, the radius (Eq. (15.32)), the Coulombic energy (Eq. (15.19)), and the energy (Eq. (15.20)) of each alkane methylene group are

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$$r_{alkaneC_{methylene} 2sp^{3}} = \frac{-e^{2}}{8\pi\varepsilon_{0} \left(E_{Coulomb} \left(C, 2sp^{3}\right) + \sum_{T_{alkane}} \left(methylene \ C - C, 2sp^{3}\right)\right)}$$

$$= \frac{e^{2}}{8\pi\varepsilon_{0} \left(e14.825751 \ eV + e0.92918 \ eV + e0.92918 \ eV\right)}$$

$$= 0.81549a_{0}$$
(15.33)

$$E_{Coulomb}\left(C_{methylene} 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}\left(0.81549a_{0}\right)} = -16.68412 \ eV \tag{15.34}$$

$$E\left(C_{methylene} 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}\left(0.81549a_{0}\right)} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}\left(0.84317a_{0}\right)^{3}} = -16.49325 \ eV \tag{15.35}$$

In the determination of the parameters of functional groups, heteroatoms bonding to $C2sp^3$ HOs to form MOs are energy matched to the $C2sp^3$ HOs. Thus, the radius and the 20 energy parameters of a bonding heteroatom are given by the same equations as those for

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 $C2sp^3$ HOs. Using Eqs. (15.15), (15.19-15.20), (15.24), and (15.32) in a generalized fashion, the final values of the radius of the HO or AO, $r_{Atom.HO.AO}$, $E_{Coulomb}$ (mol.atom, msp³), and $E\left(C_{mol}2sp^3\right)$ are calculated using $\sum E_{T_{group}}\left(MO,2sp^3\right)$, the total energy donation to each bond with which an atom participates in bonding corresponding to the values of $E_T\left(C^{BO}-C,C2sp^3\right)$ of the MO due to charge donation from the AO or HO to the MO given in Tables 15.1 and 15.2.

Table 15.3.A. The final values of $r_{Atom.HO.AO}$, $E_{Coulomb}$ (mol.atom, msp³), and $E(C_{mol}2sp^3)$ calculated using the values of $E_T(C^{BO}_T-C,C2sp^3)$ given in Tables 15.1 and 15.2.

							,						45	8															
26	25	24	23	22	21	20	19	18	17	16	15	14	13	12	11	10	9	8	7	6	5	4	W	2	1	ion	Designat	ation	Atom Hybridiz
-2.02043	-0.92918	-1.13379	-1.79278	-0.85035	-0.72457	-1.57711	-0.64574	-1.56513	-0.82688	-0.5669	-0.72457	-0.46459	-1.3725	-1.34946	-0.46459	-1.14485	-1.13379	-0.54343	-0.92918	-0.85034	-0.72457	-0.56689	-0.46459	-0.36229	0			·	$E_T \left(C - C, C2sp^3 \right)$
0	-0.92918	-0.72457	0	-0.85035	-0.92918	0	-0.92918	0	-0.72457	-0.92918	-0.72457	-0.92918	0	0	-0.82688	0	0	-0.54343	0	0	0	0	0	0	0				$ E_T \left(C - C, C2sp^3 \right) $
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0			-71144	$\left \left E_T\left(C-C,C2sp^3 ight) ight $
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0				$E_T \left(C - C, C2sp^3 \right)$
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0				$= E_T \left(C - C, C2sp^3 \right)$
0.80765	0.81549	0.81549	0.81871	0.82327	0.82562	0.82948	0.82959	0.83008	0.83078	0.8336	0.836	0.83885	0.83995	0.84115	0.84418	0.85193	0.85252	0.85503	0.86359	0.86793	0.87495	0.88392	0.88983	0.89582	0.91771			FIIIAI	Atom.HO.AO
-16.84619	-16.68412	-16.68411	-16.61853	-16.52645	-16.4/951	-16.40286	-16.40067	-16.39089	-16.37721	-16.32183	-16.2749	-16.21952	-16.19826	-16.17521	-16.11722	-15.9706	-15.95955	-15.91261	-15.75493	-15.6761	-15.55033	-15.39265	-15.29034	-15.18804	-14.82575		Final	(eV)	$E_{Coulomb}$ (mol.atom, msp 3)
-16.65532	-16.49325	-16.49325	-16.42/6/	-16.33339	-10.26603	-16.212	-10.20981	-16.20002	-16.18634	-16.13097	-16.08404	-16.02866	-16.00739	-15.98435	-15.92636	-15.7/9/4	-15./6868	-15.72175	-15.5640/	-15.48523	-15.35946	-15.20178	-15.09948	-14.99717	-14.63489			Final	$E(C_{mol}2sp^{2})$ (eV)

	· T	Γ-	т—			459 T) 		ı	Ι	Τ	1	ſ	Γ.			ı —		r	Ι	r	. 	_
50	49	48	47	46	45	4	43	42	41	40	39	38	37	36	35	34	33	32	31	30	29	28	17
-1.79278	-1.13379	-0.82688	-0.46459	-1.1338	-0.85034	-1.34946	-0.85035	-0.92918	-0.82688	-0.92918	-0.54343	-0.92918	-0.72457	-0.82688	-0.72457	-0.85035	-0.64574	-0.46459	-1.34946	-1.13379	-0.5669	-0.85035	-1.133/9
-0.92918	-1.13379	-1.34946	-0.85035	-0.92918	-0.54343	-0.64574	-0.54343	-0.92918	-0.92918	-0.85034	-0.54343	-0.72457	-0.92918	-0.72457	-0.72457	-0.5669	-0.85034	-0.92918	-0.92918	-1.13379	-0.72457	-0.85035	-0.92918
-0.92918	-1.13379	-0.92918	-0.85035	-0.92918	-0.60631	-0.92918	-0.5669	-0.92918	-0.92918	-0.85034	-0.5669	-0.92918	-0.92918	-0.92918	-0.92918	-0.92918	-0.85034	-0.92918	0	0	-0.92918	-0.46459	0
0	0	0	-0.92918	0	-0.92918	0	-0.92918	0	0	0	-0.92918	0	0	0 ,	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0.73637	0.74646	0.75877	0.75924	0.7636	0.76631	0.76652	0.76801	0.77247	0.77699	0.77945	0.78155	0.78155	0.78155	0.78617	0.79085	0.79232	0.79232	0.79340	0.79546	0.79597	0.78916	0.80076	0.80561
-18.47690	-18.22712	-17.93128	-17.92022	-17.81791	-17.75502	-17.75013	-17.71561	-17.6133	-17.51099	-17.45561	-17.40869	-17.40869	-17.40868	-17.30638	-17.20408	-17.17218	-17.17217	-17.14871	-17.1044	-17.09334	-17.04641	-16.99104	-16.88872
-18.28604	-18.03626	-17.74041	-17.72936	-17.62705	-17.56415	-17.55927	-17.52475	-17.42244	-17.32013	-17.26475	-17.21783	-17.21783	-17.21782	-17.11552	-17.01322	-16.98132	-16.98131	-16.95784	-16.91353	-16.90248	-16.85554	-16.80018	-16.69786

Table 15.3.B. The final values of $r_{Alom,HO,AO}$, $E_{Coulomb}$ (mol.atom, msp³), and $E(C_{mol}2sp^3)$ calculated for heterocyclic groups using the values of $E_T(C^{BO}_T,C_T,C_T)$ given in Tables 15.1 and 15.2.

												4	61														4
26	25	24	23	22	21	20	19	18	17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1	Designation	Atom Hybridization
-1.13379	-0.85034	-0.85034	-0.92918	-0.85034	-0.54343	-0.85035	-0.85035	-1.13379	-0.85034	-0.85035	-1.13379	-1.13379	-0.92918	-0.85035	-0.92918	-0.92918	-0.72457	-0.46459	-0.60631	-1.13379	-0.54343	-0.92918	-0.72457	-0.56690	0		$E_r \left(C - C, C2sp^3 \right)$
-0.92918	-0.54343	-0.54343	-0.92918	-0.28345	-0.54343	-0.56690	-0.54343	-1.13380	-0.85034	-0.85035	-0.92918	-0.72457	-0.92918	-0.85035	-0.72457	-0.60631	-0.72457	-0.92918	-0.60631	0	-0.54343	0	0	0	0		$E_T \left(C - C, C2sp^3 \right) E_T \left(C - C, C2sp \right)$
-0.92918	-0.60631	-0.56690	-0.92918	-0.54343	-0.56690	-0.92918	0.00000	0	-0.56690	-0.46459	0	0	0	0	0	0	0	0	0	0	0.	0	0	0	0		$E_r \left(C - C, C2sp \right)$
0	-0.92918	-0.92918	0	-0.92918	-0.92918	0	-0.92918	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		$E_T\bigg(C-C,C2sp^3$
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		$E_T \left(C - C, C2sp^3 \right)$
0.76360	0.76631	0.76801	0.77247	0.78050	0.78155	0.79232	0.79340	0.79597	0.79597	0.80076	0.80561	0.81549	0.81549	0.82327	0.82562	0.83159	0.83600	0.83885	0.84833	0.85252	0.85503	0.86359	0.87495	0.88392	0.91771	Final	YAtom.HO.AO
-17.81791	-17.75502	-17.71560	-17.61330	-17.43216	-17.40869	-17.17218	-17.14871	-17.09334	-17.09334	-16.99103	-16.88873	-16.68412	-16.68411	-16.52644	-16.47951	-16.36125	-16.27490	-16.21953	-16.03838	-15.95954	-15.91261	-15.75493	-15.55033	-15.39265	-14.82575	(eV) Final	$E_{Coulomb}$ (mol.atom, msp 3)
-17.62704	-17.56416	-17.52474	-17.42243	-17.24130	-17.21783	-16.98132	-16.95785	-16.90248	-16.90247	-16.80017	-16.69786	-16.49325	-16,49325	-16.33558	-16.28864	-16.17038	-16.08404	-16.02866	-15.84752	-15.76868	-15.72175	-15.56407	-15.35946	-15,20178	-14.63489	(eV) Final	$E\left(C_{mol}2sp^3\right)$

-1		_		_	$\overline{}$		_	_
	20	90	ţ	20		28	7.1	77
	-1.133/9	1 12220	1.1.700	1 12200	0.1010	-0 46459	1.13373	1 12270
	-1.133/9	1	-1.133/9	1 12270	-0.0000	-0 85035	-1.13500	1 12700
	-1.13379		-0.92918	00010	-0.0000	300300	-0./245/	
	0		C		-0.92918	0.00010	0	
	0		0		0	>	0	
	0.74646		0.75493		0.75924		0.76360	
	-18.22713		-18.02252		-17.92022		-17.81791	
100000	-18 03627	**:00100	-17 83166		-17.72935		-17.62705	

The energy of the MO is matched to each of the participating outermost atomic or hybridized orbitals of the bonding atoms wherein the energy match includes the energy contribution due to the AO or HO's donation of charge to the MO. The force constant k' 5 (Eq. (15.1)) is used to determine the ellipsoidal parameter c' (Eq. (15.2)) of the each H_2 -type-ellipsoidal-MO in terms of the central force of the foci. Then, c' is substituted into the energy equation (from Eq. (15.11))) which is set equal to n_1 times the total energy of H_2 where n_1 is the number of equivalent bonds of the MO and the energy of H_2 , $-31.63536831 \, eV$, Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO. From the energy equation and the relationship between the axes, the dimensions of the MO are solved. The energy equation has the semimajor axis a as it only parameter. The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each MO (Eqs. (15.3-15.5)). The parameter solutions then allow for the component and total energies of the MO to be determined.

The total energy, $E_T(\mu_2MO)$, is given by the sum of the energy terms (Eqs. (15.6-15.11)) plus $E_T(AO/HO)$:

$$E_T(H_2MO) = V_e + T + V_m + V_p + E_T(AO/HO)$$
 (15.36)

$$E_{T}(H_{2}MO) = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2}-b^{2}}} \left[c_{1}c_{2}\left(2 - \frac{a_{0}}{a}\right) \ln\frac{a + \sqrt{a^{2}-b^{2}}}{a - \sqrt{a^{2}-b^{2}}} - 1 \right] + E_{T}(AO/HO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}c'} \left[c_{1}c_{2}\left(2 - \frac{a_{0}}{a}\right) \ln\frac{a + c'}{a - c'} - 1 \right] + E_{T}(AO/HO)$$
(15.37)

where n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2 -type ellipsoidal MO basis function of a chemical bond of the group, c_2 is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of each chemical bond, and $E_T(AO/HO)$ is the total energy comprising the difference of the energy E(AO/HO) of at least one atomic or hybrid orbital to which the MO is energy matched and any energy component $\Delta E_{H_2MO}(AO/HO)$ due to the AO or HO's charge donation to the MO.

$$E_{T}(AO/HO) = E(AO/HO) - \Delta E_{H_{2}MO}(AO/HO)$$
(15.38)

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As specific examples given in previous sections, $E_T(AO/HO)$ is one from the group of

$$E_{T}(AO / HO) = E(O2p \ shell) = -E(ionization; O) = -13.6181 \ eV;$$

$$E_{T}(AO / HO) = E(N2p \ shell) = -E(ionization; N) = -14.53414 \ eV;$$

$$E_{T}(AO / HO) = E(C,2sp^{3}) = -14.63489 \ eV;$$

$$E_{T}(AO / HO) = E_{Coulomb}(Cl,3sp^{3}) = -14.60295 \ eV;$$

$$E_{T}(AO / HO) = E(ionization; C) + E(ionization; C^{+});$$

$$E_{T}(AO / HO) = E(C_{ethane}, 2sp^{3}) = -15.35946 \ eV;$$

$$E_{T}(AO / HO) = +E(C_{ethylene}, 2sp^{3}) - E(C_{ethylene}, 2sp^{3});$$

$$E_{T}(AO / HO) = E(C,2sp^{3}) - 2E_{T}(C = C,2sp^{3}) = -14.63489 \ eV - (-2.26758 \ eV);$$

$$10 \qquad E_{T}(AO / HO) = E(C_{acetylene}, 2sp^{3}) - E(C_{acetylene}, 2sp^{3}) - E(C_{acetylene}, 2sp^{3}) = 16.20002 \ eV;$$

$$E_{T}(AO / HO) = E(C,2sp^{3}) - 2E_{T}(C = C,2sp^{3}) = -14.63489 \ eV - (-3.13026 \ eV);$$

 $E_T \left(AO / HO\right) = E\left(C_{alkane}, 2sp^3\right) = -15.56407 \ eV \ .$ 15 To solve the bond parameters and energies, $c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m \ e^2 2C C \ a}} = \sqrt{\frac{aa_0}{2CC}}$ (Eq.

 $E_T(AO/HO) = E(C, 2sp^3) - E_T(C = C, 2sp^3) = -14.63489 \ eV - (-1.13379 \ eV)$, and

(15.2)) is substituted into $E_{\tau}(\mu_{2}MO)$ to give

 $E_T(AO/HO) = E(C_{henzene}, 2sp^3) - E(C_{henzene}, 2sp^3);$

$$E_{T}(H_{2}MO) = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2}-b^{2}}} \left[c_{1}c_{2} \left(2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{a^{2}-b^{2}}}{a - \sqrt{a^{2}-b^{2}}} - 1 \right] + E_{T}(AO/HO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}c'} \left[c_{1}c_{2} \left(2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + E_{T}(AO/HO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[c_{1}c_{2} \left(2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] + E_{T}(AO/HO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[c_{1}c_{2} \left(2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] + E_{T}(AO/HO)$$

The total energy is set equal to $E(basis\ energies)$ which in the most general case is given by

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the sum of a first integer n_1 times the total energy of H_2 minus a second integer n_2 times the total energy of H, minus a third integer n_3 times the valence energy of E(AO) (e.g. $E(N) = -14.53414 \ eV$) where the first integer can be 1,2,3..., and each of the second and third integers can be 0,1,2,3....

 $E(basis\ energies) = n_1 \left(-31.63536831\ eV\right) - n_2 \left(-13.605804\ eV\right) - n_3 E\left(AO\right)$ (15.40) In the case that the MO bonds two atoms other than hydrogen, $E(basis\ energies)$ is n_1 times the total energy of H_2 where n_1 is the number of equivalent bonds of the MO and the energy of H_2 , $-31.63536831\ eV$, Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO:

10
$$E(basis\ energies) = n_1 \left(-31.63536831\ eV \right)$$
 (15.41)

 $E_T(\mu_{2MO})$, is set equal to $E(basis\ energies)$, and the semimajor axis a is solved. Thus, the semimajor axis a is solved from the equation of the form:

$$-\frac{n_{1}e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}\left[c_{1}c_{2}\left(2-\frac{a_{0}}{a}\right)\ln\frac{a+\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a-\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}-1\right]+E_{T}\left(AO/HO\right)=E(basis\ energies)\ (15.42)$$

The distance from the origin of the H_2 -type-ellipsoidal-MO to each focus c', the internuclear 15 distance 2c', and the length of the semiminor axis of the prolate spheroidal H_2 -type MO b=c are solved from the semimajor axis a using Eqs. (15.2-15.4). Then, the component energies are given by Eqs. (15.6-15.9) and (15.39).

The total energy of the MO of the functional group, E_T (MO), is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms and E_T (atom – atom, msp³.AO), the change in the energy of the AOs or HOs upon forming the bond. From Eqs. (15.39-15.40), E_T (MO) is

$$E_T(MO) = E(basis\ energies) + E_T(atom - atom, msp^3.AO)$$
 (15.43)

During bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy \overline{E}_{osc} is the sum of the Doppler, \overline{E}_D , and 25 average vibrational kinetic energies, \overline{E}_{Kvib} :

$$\overline{E}_{osc} = n_1 \left(\overline{E}_D + \overline{E}_{Kvib} \right) = n_1 \left(E_{hv} \sqrt{\frac{2\overline{E}_K}{m_e c^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$
(15.44)

where n_1 is the number of equivalent bonds of the MO, k is the spring constant of the equivalent harmonic oscillator, and μ is the reduced mass. The angular frequency of the reentrant oscillation in the transition state corresponding to \overline{E}_D is determined by the force between the central field and the electrons in the transition state. The force and its derivative are given by

$$f\left(R\right) = -c_{BO} \frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3} \tag{15.45}$$

and

$$f'(a) = 2c_{BO} \frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}$$
 (15.46)

10 such that the angular frequency of the oscillation in the transition state is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{m_e}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{1o}C_{2o}e^2}{4\pi\epsilon_0 R^3}}{m_e}}$$
(15.47)

where R is the semimajor axis a or the semiminor axis b depending on the eccentricity of the bond that is most representative of the oscillation in the transition state, c_{BO} is the bond-order factor which is 1 for a single bond and when the MO comprises n_1 equivalent single bonds as in the case of functional groups. c_{BO} is 4 for an independent double bond as in the case of the CO_2 and NO_2 molecules and 9 for an independent triplet bond. C_{1o} is the fraction of the H_2 -type ellipsoidal MO basis function of the oscillatory transition state of a chemical bond of the group, and C_{2o} is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond. Typically, $C_{1o} = C_1$ and $C_{2o} = C_2$. The kinetic energy, E_K , corresponding to \overline{E}_D is given by Planck's equation for functional groups:

$$\overline{E}_{\kappa} = \hbar \omega = \hbar \sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}$$
 (15.48)

The Doppler energy of the electrons of the reentrant orbit is

$$\overline{E}_{D} \cong E_{hv} \sqrt{\frac{2\overline{E}_{K}}{m_{e}c^{2}}} = E_{hv} \sqrt{\frac{2\hbar \sqrt{\frac{\overline{C_{1o}C_{2o}e^{2}}}{4\pi\varepsilon_{0}R^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}}$$

$$(15.49)$$

 \overline{E}_{osc} given by the sum of \overline{E}_{D} and $\overline{E}_{K\!\nu ib}$ is

$$\overline{E}_{osc}(group) = n_1 \left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1 \left(E_{hv} \sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e} + E_{vib}}\right) \tag{15.50}$$

 E_{hv} of a group having n_1 bonds is given by $E_T(MO)/n_1$ such that

$$\overline{E}_{osc} = n_1 \left(\overline{E}_D + \overline{E}_{Kvib} \right) = n_1 \left(E_T \left(MO \right) / n_1 \sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$
 (15.51)

 E_{T+osc} (Group) is given by the sum of E_T (MO) (Eq. (15.42)) and \overline{E}_{osc} (Eq. (15.51)):

$$\begin{split} E_{T+osc} & (Group) = E_T (MO) + \overline{E}_{osc} \\ & = \begin{pmatrix} -\frac{n_1 e^2}{8\pi\varepsilon_0 \sqrt{\frac{aa_0}{2C_1C_2}}} & c_1c_2 \left(2 - \frac{a_0}{a}\right) \ln \frac{a + \sqrt{\frac{aa_0}{2C_1C_2}}}{a - \sqrt{\frac{aa_0}{2C_1C_2}}} - 1 \\ + E_T \left(AO / HO\right) + E_T \left(atom - atom, msp^3.AO\right) \end{pmatrix} \\ & = \begin{pmatrix} -\frac{n_1 e^2}{8\pi\varepsilon_0 \sqrt{\frac{aa_0}{2C_1C_2}}} & c_1c_2 \left(2 - \frac{a_0}{a}\right) \ln \frac{a + \sqrt{\frac{aa_0}{2C_1C_2}}}{a - \sqrt{\frac{aa_0}{2C_1C_2}}} - 1 \\ + E_T \left(AO / HO\right) + E_T \left(atom - atom, msp^3.AO\right) \end{pmatrix} \\ & = \begin{pmatrix} -\frac{n_1 e^2}{8\pi\varepsilon_0 \sqrt{\frac{aa_0}{2C_1C_2}}} & -1 \\ -\frac{aa_0}{2C_1C_2} & -1$$

$$= \left(E(basis\ energies) + E_T\left(atom-atom, msp^3.AO\right)\right) \\ 1 + \sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{\frac{m_e}{m_e}}}\right] + n_1 \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

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The total energy of the functional group E_T (group) is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms, $E(basis\ energies)$, the change in the energy of the AOs or HOs upon forming the bond (E_T (atom – atom, msp^3 .AO)), the energy of oscillation in the transition state, and the change in magnetic energy with bond formation, E_{mag} . From Eq. (15.52), the total energy of the group E_T (Group) is

$$E_{T}(Group) = \left(E(basis\ energies) + E_{T}(atom-atom, msp^{3}.AO)\right)\left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}}\right]\right) (15.53)$$

The change in magnetic energy E_{mag} which arises due to the formation of unpaired electrons in the corresponding fragments relative to the bonded group is given by

10
$$E_{mag} = c_3 \frac{2\pi\mu_0 e^2\hbar^2}{m_s^2 r^3} = c_3 \frac{8\pi\mu_0 \mu_B^2}{r^3}$$
 (15.54)

where r^3 is the radius of the atom that reacts to form the bond and c_3 is the number of electron pairs.

$$E_{T} (Group) = \left(E(basis\ energies) + E_{T} \left(atom - atom, msp^{3}.AO\right)\right) \left[1 + \sqrt{\frac{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}{m_{e}}}\right] + n_{1}\overline{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}}$$

$$(15.55)$$

The total bond energy of the group E_D (Group) is the negative difference of the total energy of the group (Eq. (15.55)) and the total energy of the starting species given by the sum of $c_4 E_{initial}$ ($c_4 AO/HO$) and $c_5 E_{initial}$ ($c_5 AO/HO$):

$$E_{D} (Group) = -\left(E(basis\ energies) + E_{T} \left(atom - atom, msp^{3}.AO\right) \left[1 + \sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}} \frac{1}{m_{e}}\right] + n_{1}\overline{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r_{n}^{3}} - \left(c_{4}E_{initial}\left(AO/HO\right) + c_{5}E_{initial}\left(c_{5}AO/HO\right)\right)\right)$$

$$(15.56)$$

In the case of organic molecules, the atoms of the functional groups are energy matched to the $C2sp^3$ HO such that

$$E(AO/HO) = -14.63489 eV$$
 (15.57)

5 For examples of E_{mag} from previous sections:

$$E_{mag}\left(C2sp^{3}\right) = c_{3} \frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}} = c_{3} \frac{8\pi\mu_{o}\mu_{B}^{2}}{\left(0.91771a_{0}\right)^{3}} = c_{3}0.14803 \ eV \tag{15.58}$$

$$E_{mag}\left(O2p\right) = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{a_0^3} = c_3 0.11441 \ eV \tag{15.59}$$

$$E_{mag}(N2p) = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{\left(0.93084a_0\right)^3} = c_3 0.14185 \ eV$$
 (15.60)

In the general case of the solution of an organic functional group, the geometric bond parameters are solved from the semimajor axis and the relationships between the parameters by first using Eq. (15.42) to arrive at a. Then, the remaining parameters are determined using Eqs. (15.1-15.5). Next, the energies are given by Eqs. (15.52-15.59). To meet the equipotential condition for the union of the H_2 -type-ellipsoidal-MO and the HO or AO of the atom of a functional group, the factor c_2 of a H_2 -type ellipsoidal MO in principal Eqs. (15.42) and (15.52) may given by

(i) one:
$$c_2 = 1$$
 (15.61)

20 (ii) the ratio that is less than one of $13.605804 \, eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), and the magnitude of the

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Coulombic energy of the participating AO or HO of the atom, $E_{Coulomb} \left(MO.atom, msp^3 \right)$ given by Eqs. (15.19) and (15.31-15.32). For $\left| E_{Coulomb} \left(MO.atom, msp^3 \right) \right>$ 13.605804 eV:

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-B\ AorBsp^{3}}}} = \frac{13.605804\ eV}{\left|E_{Coulomb}\left(MO.atom, msp^{3}\right)\right|}$$
(15.62)

For $\left|E_{Coulomb}\left(MO.atom, msp^{3}\right)\right| < 13.605804 \ eV$:

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-B\ AorBsp^{3}}}}{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}} = \frac{\left|E_{Coulomb}\left(MO.atom, msp^{3}\right)\right|}{13.605804\ eV}$$
(15.63)

(iii) the ratio that is less than one of 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), and the magnitude of the valence energy, E(valence), of the participating AO or HO of the atom where E(valence) is 10 the ionization energy or $E(MO.atom, msp^3)$ given by Eqs. (15.20) and (15.31-15.32). For $|E(valence)| > 13.605804 \ eV$:

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-B\ AorBsp^{3}}}} = \frac{13.605804\ eV}{|E(valence)|}$$
(15.64)

For |E(valence)| < 13.605804 eV:

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-B\ AorBsp^{3}}}}{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}} = \frac{|E(valence)|}{13.605804\ eV}$$
(15.65)

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(iv) the ratio that is less than one of the magnitude of the Coulombic energy of the participating AO or HO of a first atom, $E_{Coulomb} \left(MO.atom, msp^3\right)$ given by Eqs. (15.19) and (15.31-15.32), and the magnitude of the valence energy, E(valence), of the participating AO or HO of a second atom to which the first is energy matched where E(valence) is the

ionization energy or $E(MO.atom, msp^3)$ given by Eqs. (15.20) and (15.31-15.32). For $|E_{Coulomb}(MO.atom, msp^3)\rangle > E(valence)$:

$$c_2 = \frac{|E(valence)|}{\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|}$$
(15.66)

For $|E_{Coulomb}(MO.atom, msp^3)| < E(valence)$:

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$$c_2 = \frac{\left| E_{Coulomb} \left(MO.atom, msp^3 \right) \right|}{\left| E(valence) \right|}$$
 (15.67)

(v) the ratio that is less than one of the magnitude of the valence-level energies, $E_n(valence)$, of the AO or HO of the nth participating atom of two that are energy matched where E(valence) is the ionization energy or $E(MO.atom, msp^3)$ given by Eqs. (15.20) and 10 (15.31-15.32):

$$c_2 = \frac{E_1(valence)}{E_2(valence)}$$
 (15.68)

(vi) the factor that is the ratio of the hybridization factor $c_2(1)$ of the valence AO or HO of a first atom and the hybridization factor $c_2(2)$ of the valence AO or HO of a second atom to which the first is energy matched where $c_2(n)$ is given by Eqs. (15.62-15.68); alternatively c_2 is the hybridization factor $c_2(1)$ of the valence AOs or HOs a first pair of atoms and the hybridization factor $c_2(2)$ of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = \frac{c_2(1)}{c_2(2)} \tag{15.69}$$

(vii) the factor that is the product of the hybridization factor $c_2(1)$ of the valence AO or HO of a first atom and the hybridization factor $c_2(2)$ of the valence AO or HO of a second atom to which the first is energy matched where $c_2(n)$ is given by Eqs. (15.62-15.69);

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alternatively c_2 is the hybridization factor $c_2(1)$ of the valence AOs or HOs a first pair of atoms and the hybridization factor $c_2(2)$ of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = c_2(1)c_2(2) (15.70)$$

5 The hybridization factor c_2 corresponds to the force constant k (Eqs. (11.65) and (13.58)). In the case that the valence or Coulombic energy of the AO or HO is less than 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), then C_2 corresponding to k' (Eq. (15.1)) is given by Eqs. (15.62-15.70).

Specific examples of the factors c_2 and C_2 of a H_2 -type ellipsoidal MO of Eq. 10 (15.51) given in following sections are

$$c_{2}(C2sp^{3}HO \ to \ F) = \frac{E(C,2sp^{3})}{E(F)}c_{2}(C2sp^{3}HO) = \frac{-14.63489 \ eV}{-17.42282 \ eV}(0.91771) = 0.77087;$$

$$C_{2}(C2sp^{3}HO \ to \ Cl) = \frac{E(Cl)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-12.96764 \ eV}{-14.63489 \ eV}(0.91771) = 0.81317;$$

$$C_{2}(C2sp^{3}HO \ to \ Br) = \frac{E(Br)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-11.81381 \ eV}{-14.63489 \ eV}(0.91771) = 0.74081;$$

$$C_{2}(C2sp^{3}HO \ to \ I) = \frac{E(I)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-10.45126 \ eV}{-14.63489 \ eV}(0.91771) = 0.65537;$$

$$15 \qquad c_{2}(C2sp^{3}HO \ to \ O) = \frac{E(O)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-13.61806 \ eV}{-14.63489 \ eV}(0.91771) = 0.85395;$$

$$c_{2}(H \ to \ 1^{\circ}N) = \frac{E(N)}{E(C,2sp^{3})} = \frac{-14.53414 \ eV}{-15.35946 \ eV} = 0.94627;$$

$$c_{2}(C2sp^{3}HO \ to \ N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-14.53414 \ eV}{-14.63489 \ eV}(0.91771) = 0.91140;$$

$$c_{2}(H \ to \ 2^{\circ}N) = \frac{E(N)}{E(C,2sp^{3})} = \frac{-14.53414 \ eV}{-15.56407 \ eV} = 0.93383;$$

$$C_{2}(S3p \ to \ H) = \frac{E(S)}{E(H)} = \frac{-10.36001 \ eV}{-13.60580 \ eV} = 0.76144;$$

$$20 \qquad C_{2}(C2sp^{3}HO \ to \ S) = \frac{E(S)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-10.36001 \ eV}{-14.63489 \ eV}(0.91771) = 0.64965;$$

$$c_{2}(O \text{ to } S3sp^{3} \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(S)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}}(0.91771);$$

$$= 1.20632$$

$$c_{2}(S3sp^{3}) = \frac{E_{Coulomb}(S3sp^{3})}{E(H)} = \frac{-11.57099 \text{ eV}}{-13.60580 \text{ eV}} = 0.85045;$$

$$C_{2}(C2sp^{3}HO \text{ to } S3sp^{3}) = \frac{E(S3sp^{3})}{E(C,2sp^{3})}c_{2}(S3sp^{3}) = \frac{-11.52126 \text{ eV}}{-14.63489 \text{ eV}}(0.85045) = 0.66951;$$

$$C_{2}(S3sp^{3} \text{ to } O \text{ to } C2sp^{3}HO) = \frac{E(S,3sp^{3})}{E(O,2p)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-11.52126 \text{ eV}}{-13.61806 \text{ eV}}(0.91771);$$

$$= 0.77641$$

$$c_{2}(O \text{ to } N2p \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(N)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-14.53414 \text{ eV}}(0.91771);$$

$$= 0.85987$$

$$c_{2}(N2p \text{ to } O2p) = \frac{c_{2}(C2sp^{2}HO \text{ to } N)}{c_{2}(C2sp^{3}HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727;$$

$$C_{2}(benzeneC2sp^{2}HO) = c_{2}(benzeneC2sp^{3}HO) = \frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252;$$

$$c_{2}(arylC2sp^{3}HO \text{ to } O) = \frac{E(O)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-14.63489 \text{ eV}}(0.85252) \qquad ;$$

$$= 0.79329$$

$$c_{2}(H \text{ to anline } N) = \frac{E(N)}{E(C,2sp^{3})} = \frac{-14.53414 \text{ eV}}{-15.76868 \text{ eV}} = 0.92171;$$

$$c_{2}(arylC2sp^{3}HO \ to \ N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$
$$= \frac{-14.53414 \ eV}{-14.63489 \ eV}(0.85252) ,$$

= 0.84665

and

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$$C_2 \left(S3p \text{ to aryl-type } C2sp^3 HO \right) = \frac{E(S, 3p)}{E(C, 2sp^3)} = \frac{-10.36001 \text{ eV}}{-15.76868 \text{ eV}} = 0.65700.$$

MO INTERCEPT ANGLES AND DISTANCES

Consider the general case of Eqs. (13.84-13.95) wherein the nucleus of a B atom and the 5 nucleus of a A atom comprise the foci of each H_2 -type ellipsoidal MO of an A-B bond. The parameters of the point of intersection of each H_2 -type ellipsoidal MO and the A-atom AO are determined from the polar equation of the ellipse:

$$r = r_0 \frac{1+e}{1+e\cos\theta'} \tag{15.71}$$

The radius of the A shell is r_A , and the polar radial coordinate of the ellipse and the radius of the A shell are equal at the point of intersection such that

$$r_A = \left(a - c'\right) \frac{1 + \frac{c'}{a}}{1 + \frac{c'}{a}\cos\theta'} \tag{15.72}$$

The polar angle θ' at the intersection point is given by

$$\theta' = \cos^{-1} \left(\frac{a}{c'} \left((a - c') \frac{1 + \frac{c'}{a}}{a_0} - 1 \right) \right)$$
 (15.73)

Then, the angle θ_{AAO} the radial vector of the A AO makes with the internuclear axis is

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$$\theta_{AAO} = 180^{\circ} - \theta'$$
 (15.74)

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals such that the angle $\omega t = \theta_{H_2MO}$ between the internuclear axis and the point of intersection of each H_2 -type ellipsoidal MO with the A radial vector obeys the following relationship:

$$r_A \sin \theta_{AAO} = b \sin \theta_{H_2MO} \tag{15.75}$$

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{r_a \sin \theta_{AAO}}{h} \tag{15.76}$$

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The distance d_{H_2MO} along the internuclear axis from the origin of H_2 -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H,MO} = a\cos\theta_{H,MO} \tag{15.77}$$

The distance d_{AAO} along the internuclear axis from the origin of the A atom to the point of 5 intersection of the orbitals is given by

$$d_{AAO} = c' - d_{H,MO} (15.78)$$

BOND ANGLES

Further consider an ACB MO comprising a linear combination of C-A-bond and C-B10 bond MOs where C is the general central atom. A bond is also possible between the A and B atoms of the C-A and C-B bonds. Such A-B bonding would decrease the C-A and C-B bond strengths since electron density would be shifted from the latter bonds to the former bond. Thus, the $\angle ACB$ bond angle is determined by the condition that the total energy of the H_2 -type ellipsoidal MO between the terminal A and B atoms is zero. The 15 force constant k' of a H_2 -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\varepsilon_a} \tag{15.79}$$

where C_1 is the fraction of the H_2 -type ellipsoidal MO basis function of a chemical bond of the molecule which is 0.75 (Eq. (13.59)) for a terminal A - H (A is H or other atom) and 1 20 otherwise and C_2 is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the chemical bond and is equal to the corresponding factor of Eqs. (15.42) and (15.52). The distance from the origin of the MO to each focus c' of the A - B ellipsoidal MO is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}}$$
 (15.80)

25 The internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.81}$$

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The length of the semiminor axis of the prolate spheroidal A - B MO b = c is given by Eq. (15.4).

The component energies and the total energy, $E_T(\mu_2 Mo)$, of the A-B bond are given by the energy equations (Eqs. (11.207-11.212), (11.213-11.217), and (11.239)) of H_2 except 5 that the terms based on charge are multiplied by c_{BO} , the bond-order factor which is 1 for a single bond and when the MO comprises n_1 equivalent single bonds as in the case of functional groups. c_{BO} is 4 for an independent double bond as in the case of the CO_2 and NO_2 molecules. The kinetic energy term is multiplied by c'_{BO} which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond. The electron energy terms are multiplied by c_1 , 10 the fraction of the H_2 -type ellipsoidal MO basis function of a terminal chemical bond which is 0.75 (Eq. (13.233)) for a terminal A-H (A is H or other atom) and 1 otherwise. The electron energy terms are further multiplied by c'_2 , the hybridization or energy-matching factor that results in an equipotential energy match of the participating at least two atomic orbitals of each terminal bond. Furthermore, when A-B comprises atoms other than H, 15 E_T (atom – atom, msp³.AO), the energy component due to the AO or HO's charge donation to the terminal MO, is added to the other energy terms to give E_T ($\mu_2 MO$):

$$E_{T}(H_{2MO}) = \frac{-e^{2}}{8\pi\varepsilon_{0}c'} \left[c_{1}c'_{2} \left(2c_{BO} - c'_{BO} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] + E_{T} \left(atom - atom, msp^{3}.AO \right)$$
(15.82)

The radiation reaction force in the case of the vibration of A-B in the transition state 20 corresponds to the Doppler energy, E_D , given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. The total energy that includes the radiation reaction of the A-B MO is given by the sum of $E_T(\mu_{2MO})$ (Eq. (15.82)) and \overline{E}_{osc} given Eqs. (11.213-11.220), (11.231-11.236), and (11.239-11.240). Thus, the total energy $E_T(A-B)$ of the A-B MO including the Doppler term is

$$E_{T}(A-B) = \begin{bmatrix} \left(\frac{-e^{2}}{8\pi\varepsilon_{0}c'} \left[c_{1}c'_{2}\left(2c_{BO} - c'_{BO}\frac{a_{0}}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] + E_{T}\left(atom - atom, msp^{3}.AO\right) \right] \\ \left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{c_{BO}\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}a^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}}\right] + \frac{1}{2}\hbar\sqrt{\frac{c_{BO}\frac{c_{1}c'_{2}e^{2}}{8\pi\varepsilon_{o}a^{3}} - \frac{c_{BO}e^{2}}{8\pi\varepsilon_{o}(a+c')^{3}}}{\mu}} \\ (15.83)$$

where C_{1o} is the fraction of the H_2 -type ellipsoidal MO basis function of the oscillatory transition state of the A-B bond which is 0.75 (Eq. (13.233)) in the case of H bonding to a central atom and 1 otherwise, C_{2o} is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond, and $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the nuclei given by Eq. (11.154). To match the boundary condition that the total energy of the A-B ellipsoidal MO is zero, $E_T (A-B)$ given by Eq. (15.83) is set equal to zero. Substitution of Eq. (15.81) into Eq. (15.83) gives

$$10 \quad 0 = \begin{bmatrix} \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} c_{1}c_{2}'\left(2c_{BO} - c'_{BO}\frac{a_{0}}{a}\right) \ln\frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] + E_{T}\left(atom - atom, msp^{3}.AO\right) \\ \left[\frac{2\hbar\sqrt{\frac{c_{1}C_{2}e^{2}}{4\pi\varepsilon_{0}a^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}} \right] + \frac{1}{2}\hbar\sqrt{\frac{c_{1}C_{2}'e^{2}}{8\pi\varepsilon_{0}a^{3}} - \frac{c_{BO}e^{2}}{8\pi\varepsilon_{0}a^{3}}}{\mu}}$$

$$= \frac{\left[\frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] + E_{T}\left(atom - atom, msp^{3}.AO\right)}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] + E_{T}\left(atom - atom, msp^{3}.AO\right)$$

$$= \frac{\left[\frac{aa_{0}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] + E_{T}\left(atom - atom, msp^{3}.AO\right)}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] + E_{T}\left(atom - atom, msp^{3}.AO\right)$$

$$= \frac{\left[\frac{aa_{0}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] + E_{T}\left(atom - atom, msp^{3}.AO\right)}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] + E_{T}\left(atom - atom, msp^{3}.AO\right)$$

The vibrational energy-term of Eq. (15.84) is determined by the forces between the central field and the electrons and those between the nuclei (Eqs. (11.141-11.145)). The electron-central-field force and its derivative are given by

15
$$f(a) = -c_{BO} \frac{c_1 c_2' e^2}{4\pi \varepsilon_0 a^3}$$
 (15.85)

and

$$f'(a) = 2c_{BO} \frac{c_1 c_2' e^2}{4\pi\varepsilon_0 a^3}$$
 (15.86)

The nuclear repulsion force and its derivative are given by

$$f\left(a+c^{\dagger}\right) = \frac{e^{2}}{8\pi\varepsilon_{o}\left(a+c^{\dagger}\right)^{2}} \tag{15.87}$$

and

5

$$f'(a+c') = -\frac{e^2}{4\pi\varepsilon_o(a+c')^3}$$
 (15.88)

such that the angular frequency of the oscillation is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{\mu}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_1c_2'e^2}{4\pi\varepsilon_0a^3} - \frac{e^2}{8\pi\varepsilon_0(a+c')^2}}{\mu}}$$
(15.89)

Since both terms of $\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib}$ are small due to the large values of a and c', to very good approximation, a convenient form of Eq. (15.84) which is evaluated to determine the bond angles of functional groups is given by

$$0 = \begin{bmatrix} \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[c_{1}c_{2}'\left(2 - \frac{a_{0}}{a}\right)\ln\frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1\right] + E_{T}\left(atom - atom, msp^{3}.AO\right) \\ \left[\frac{1 + \sqrt{\frac{c_{1}e^{2}}{4\pi\varepsilon_{0}a^{3}}}}{\frac{aa_{0}}{m_{e}}} + \frac{1}{2}\hbar\sqrt{\frac{c_{1}e^{2}}{8\pi\varepsilon_{0}a^{3}}} + \frac{e^{2}}{8\pi\varepsilon_{0}\left(a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}\right)^{3}}} \right] + \frac{1}{2}\hbar\sqrt{\frac{aa_{0}}{m_{e}c^{2}}} + \frac{1}{2}\hbar\sqrt{\frac{aa_{0}}{8\pi\varepsilon_{0}a^{3}}} + \frac{1}{2}\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}} +$$

From the energy relationship given by Eq. (15.90) and the relationship between the axes given by Eqs. (15.2-15.5), the dimensions of the A-B MO can be solved. The most convenient way to solve Eq. (15.90) is by the reiterative technique using a computer.

A factor c_2 of a given atom in the determination of c_2' for calculating the zero of the total A-B bond energy is typically given by Eqs. (15.62-15.65). In the case of a H-H terminal bond of an alkyl or alkenyl group, c_2' is typically the ratio of c_2 of Eq. (15.62) for the H-H bond which is one and c_2 of the carbon of the corresponding C-H bond:

$$c_2' = \frac{1}{c_2(C2sp^3)} = \frac{13.605804 \, eV}{E_{Coulomb} \left(C - H \, C2sp^3\right)}$$
(15.91)

In the case of the determination of the bond angle of the ACH MO comprising a linear combination of C-A-bond and C-H-bond MOs where A and C are general, C is the central atom, and c_2 for an atom is given by Eqs. (15.62-15.70), c_2' of the A-H terminal bond is typically the ratio of c_2 of the A atom for the A-H terminal bond and c_2 of the C atom of the corresponding C-H bond:

$$c_2' = \frac{c_2(A(A-H)msp^3)}{c_2(C(C-H)(msp^3)}$$
(15.92)

In the case of the determination of the bond angle of the COH MO of an alcohol comprising a linear combination of C-O-bond and O-H-bond MOs where C, O, and H are carbon, oxygen, and hydrogen, respectively, c'_2 of the C-H terminal bond is typically 0.91771 since the oxygen and hydrogen atoms are at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively) that is energy matched to the $C2sp^3$ HO.

In the determination of the hybridization factor c_2' of Eq. (15.90) from Eqs. (15.62-15.70), the Coulombic energy, $E_{Coulomb} \left(MO.atom, msp^3 \right)$, or the energy, $E \left(MO.atom, msp^3 \right)$, 15 the radius $r_{A-B.AorBsp^3}$ of the A or B AO or HO of the heteroatom of the A-B terminal bond MO such as the $C2sp^3$ HO of a terminal C-C bond is calculated using Eq. (15.32) by considering $\sum E_{T_{mol}} \left(MO, 2sp^3 \right)$, the total energy donation to each bond with which it participates in bonding as it forms the terminal bond. The Coulombic energy $E_{Coulomb} \left(MO.atom, msp^3 \right)$ of the outer electron of the $atom\ msp^3$ shell is given by Eq. (15.19). 20 In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy $E\left(MO.atom, msp^3 \right)$ of the outer electron of the $atom\ msp^3$ shell is given by the sum of $E_{Coulomb} \left(MO.atom, msp^3 \right)$ and E(magnetic) (Eq. (15.20)).

In the specific case of the terminal bonding of two carbon atoms, the c_2 factor of each carbon given by Eq. (15.62) is determined using the Coulombic energy $E_{Coulomb} \left(C - C \ C2sp^3 \right)$ of the outer electron of the $C2sp^3$ shell given by Eq. (15.19) with the

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radius $r_{C-C\ C2sp^3}$ of each $C2sp^3$ HO of the terminal C-C bond calculated using Eq. (15.32) by considering $\sum E_{T_{mol}}\left(MO,2sp^3\right)$, the total energy donation to each bond with which it participates in bonding as it forms the terminal bond including the contribution of the methylene energy, 0.92918 eV (Eq. (14.513)), corresponding to the terminal C-C bond. The corresponding $E_{-}\left(atom-atom\ msp^3\ AO\right)$ in Fig. (15.90)

5 The corresponding
$$E_T$$
 (atom – atom, msp³.AO) in Eq. (15.90) is
$$E_T \left(C - C C 2sp^3\right) = -1.85836 \ eV.$$

In the case that the terminal atoms are carbon or other heteroatoms, the terminal bond comprises a linear combination of the HOs or AOs; thus, c'_2 is the average of the hybridization factors of the participating atoms corresponding to the normalized linear sum:

10
$$c'_2 = \frac{1}{2} \left(c'_2 \left(atom \ 1 \right) + c'_2 \left(atom \ 2 \right) \right)$$
 (15.93)

In the exemplary cases of C-C, O-O, and N-N where C is carbon:

$$c_{2}' = \frac{1}{2} \left(\frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-AA_{1}AO/HO}}} + \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-AA_{2}AO/HO}}} \right)$$

$$= \frac{1}{2} \left(\frac{13.605804 \ eV}{E_{Coulomb} \left(A - A.A_{1}AO/HO \right)} + \frac{13.605804 \ eV}{E_{Coulomb} \left(A - A.A_{2}AO/HO \right)} \right)$$
(15.94)

In the exemplary cases of C - N, C - O, and C - S,

$$c_2' = \frac{1}{2} \left(\frac{13.605804 \ eV}{E_{Coulomb} \left(C - B \ C2sp^3 \right)} + c_2 \left(C \ to \ B \right) \right)$$
 (15.95)

where C is carbon and $c_2(C \text{ to } B)$ is the hybridization factor of Eqs. (15.52) and (15.84) that matches the energy of the atom B to that of the atom C in the group. For these cases, the corresponding $E_T(atom-atom,msp^3.AO)$ term in Eq. (15.90) depends on the hybridization and bond order of the terminal atoms in the molecule, but typical values matching those used in the determination of the bond energies (Eq. (15.56)) are

$$E_{T}\left(C - O C2sp^{3}.O2p\right) = -1.44915 \ eV; \qquad E_{T}\left(C - O C2sp^{3}.O2p\right) = -1.65376 \ eV;$$

$$E_{T}\left(C - N C2sp^{3}.N2p\right) = -1.44915 \ eV; \qquad E_{T}\left(C - S C2sp^{3}.S2p\right) = -0.72457 \ eV;$$

$$E_{T}\left(O - O O2p.O2p\right) = -1.44915 \ eV; \qquad E_{T}\left(O - O O2p.O2p\right) = -1.65376 \ eV;$$

$$E_{T}(N-N N2p.N2p) = -1.44915 \ eV; \qquad E_{T}(N-O N2p.O2p) = -1.44915 \ eV;$$

$$E_{T}(F-F F2p.F2p) = -1.44915 \ eV; \qquad E_{T}(Cl-Cl Cl3p.Cl3p) = -0.92918 \ eV;$$

$$E_{T}(Br-Br Br4p.Br4p) = -0.92918 \ eV; \qquad E_{T}(I-I I5p.I5p) = -0.36229 \ eV;$$

$$E_{T}(C-F C2sp^{3}.F2p) = -1.85836 \ eV; \qquad E_{T}(C-Cl C2sp^{3}.Cl3p) = -0.92918 \ eV;$$

$$E_{T}(C-Cl C2sp^{3}.Sl3p) = -0.92918 \ eV; \qquad E_{T}(C-I C2sp^{3}.I5p) = -0.36228 \ eV; \qquad eV;$$

$$E_{T}(C-Cl C2sp^{3}.I5p) = -0.36228 \ eV; \qquad eV;$$

$$E_{T}(C-Cl C2sp^{3}.I5p) = -0.36228 \ eV; \qquad eV;$$

In the case that the terminal bond is X-X where X is a halogen atom, c_1 is one, and c_2' is the average (Eq. (15.93)) of the hybridization factors of the participating halogen atoms given by Eqs. (15.62-15.63) where $E_{Coulomb}\left(MO.atom, msp^3\right)$ is determined using Eq. (15.32) and $E_{Coulomb}\left(MO.atom, msp^3\right)=13.605804\ eV$ for X=I. The factor C_1 of Eq. (15.90) is one for all halogen atoms. The factor C_2 of fluorine is one since it is the only halogen wherein the ionization energy is greater than that 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). For each of the other halogens, Cl, Br, and I, C_2 is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with $c_2(1)$ being that of the halogen given by Eq. (15.68) that matches the valence energy of X ($E_1(valence)$) to that of the $C2sp^3$ HO ($C_2(valence)=-14.63489\ eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO ($c_2(2)=0.91771$, Eq. (13.430)). $E_T(atom-atom, msp^3.AO)$ of Eq. (15.90) is the maximum for the participating atoms which is $-1.44915\ eV$, $-0.92918\ eV$, $-0.92918\ eV$, and $-0.33582\ eV$ for F, Cl, Br, and I, C_2 0 respectively.

Consider the case that the terminal bond is C-X where C is a carbon atom and X is a halogen atom. The factors c_1 and c_2 of Eq. (15.90) are one for all halogen atoms. For X=F, c_2' is the average (Eq. (15.95)) of the hybridization factors of the participating carbon and F atoms where c_2 for carbon is given by Eq. (15.62) and c_2 for fluorine matched to carbon is given by Eq. (15.70) with c_2 (1) for the fluorine atom given by Eq. (15.68) that matches the valence energy of F (E_1 (valence) = -17.42282 eV) to that of the $C2sp^3$ HO

 $(E_2(valence) = -14.63489 \, eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO $(c_2(2) = 0.91771, \, \text{Eq.} (13.430))$. The factor C_2 of fluorine is one since it is the only halogen wherein the ionization energy is greater than that 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). For each of 5 the other halogens, CI, Br, and I, c_2' is the hybridization factor of the participating carbon atom since the halogen atom is energy matched to the carbon atom. C_2 of the terminal-atom bond matches that used to determine the energies of the corresponding C-X-bond MO. Then, C_2 is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with $c_2(1)$ for the halogen atom given by Eq. (15.68) that matches the valence energy of X ($E_1(valence)$) to 10 that of the $C2sp^3$ HO ($E_2(valence) = -14.63489 \, eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO ($c_2(2) = 0.91771$, Eq. (13.430)). $E_T(atom - atom, msp^3.AO)$ of Eq. (15.90) is the maximum for the participating atoms which is $-1.85836 \, eV$, $-0.92918 \, eV$, $-0.72457 \, eV$, and $-0.33582 \, eV$ for F, CI, Br, and I, respectively.

Consider the case that the terminal bond is H-X corresponding to the angle of the atoms HCX where C is a carbon atom and X is a halogen atom. The factors c_1 and C_1 of Eq. (15.90) are 0.75 for all halogen atoms. For X=F, c_2' is given by Eq. (15.69) with c_2 of the participating carbon and F atoms given by Eq. (15.62) and Eq. (15.65), respectively. The factor C_2 of fluorine is one since it is the only halogen wherein the ionization energy is greater than that 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). For each of the other halogens, CI, Br, and I, c_2' is also given by Eq. (15.69) with c_2 of the participating carbon given by Eq. (15.62) and c_2 of the participating X atom given by $c_2 = 0.91771$ (Eq. (13.430)) since the X atom is energy matched to the $C2sp^3$ HO. In these cases, C_2 is given by Eq. (15.65) for the corresponding atom X where C_2 matches the energy of the atom X to that of H.

Using the distance between the two atoms A and B of the general molecular group ACB when the total energy of the corresponding A-B MO is zero, the corresponding bond angle can be determined from the law of cosines:

$$s_1^2 + s_2^2 - 2s_1 s_2 \cos ine \theta = s_3^2$$
 (15.96)

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With $s_1 = 2c'_{C-A}$, the internuclear distance of the C-A bond, $s_2 = 2c'_{C-B}$, the internuclear distance of each C-B bond, and $s_3 = 2c'_{A-B}$, the internuclear distance of the two terminal atoms, the bond angle $\theta_{\angle ACB}$ between the C-A and C-B bonds is given by

$$(2c'_{C-A})^2 + (2c'_{C-B})^2 - 2(2c'_{C-A})(2c'_{C-B})\cos \theta = (2c'_{A-B})^2$$
(15.97)

$$\theta_{\angle ACB} = \cos^{-1} \left(\frac{(2c'_{C-A})^2 + (2c'_{C-B})^2 - (2c'_{A-B})^2}{2(2c'_{C-A})(2c'_{C-B})} \right)$$
(15.98)

Consider the exemplary structure $C_bC_a(O_a)O_b$ wherein C_a is bound to C_b , O_a , and O_b . In the general case that the three bonds are coplanar and two of the angles are known, say θ_1 and θ_2 , then the third θ_3 can be determined geometrically:

$$\theta_3 = 360 - \theta_1 - \theta_2 \tag{15.99}$$

10 In the general case that two of the three coplanar bonds are equivalent and one of the angles is known, say θ_1 , then the second and third can be determined geometrically:

$$\theta_2 = \theta_3 = \frac{(360 - \theta_1)}{2} \tag{15.100}$$

ANGLES AND DISTANCES FOR AN MO THAT FORMS AN ISOSCELES 15 TRIANGLE

In the general case where the group comprises three A-B bonds having B as the central atom at the apex of a pyramidal structure formed by the three bonds with the A atoms at the base in the xy-plane. The $C_{3\nu}$ axis centered on B is defined as the vertical or z-axis, and any two A-B bonds form an isosceles triangle. Then, the angle of the bonds and the distances from and along the z-axis are determined from the geometrical relationships given by Eqs. (13.412-13.416):

the distance $d_{origin-B}$ from the origin to the nucleus of a terminal B atom is given by

$$d_{origin-B} = \frac{2c'_{B-B}}{2\sin 60^{\circ}} \tag{15.101}$$

the height along the z-axis from the origin to the A nucleus $d_{{\scriptscriptstyle height}}$ is given by

25
$$d_{height} = \sqrt{(2c'_{A-B})^2 - (d_{origin-B})^2}$$
, and (15.102)

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the angle θ_{ν} of each A-B bond from the z-axis is given by

$$\theta_{v} = \tan^{-1} \left(\frac{d_{origin-B}}{d_{height}} \right) \tag{15.103}$$

Consider the case where the central atom B is further bound to a fourth atom C and the B-C bond is along the z-axis. Then, the bond $\theta_{\angle ABC}$ given by Eq. (14.206) is

$$\theta_{\angle ABC} = 180 - \theta_{v} \tag{15.104}$$

DIHEDRAL ANGLE

Consider the plane defined by a general ACA MO comprising a linear combination of two C-A-bond MOs where C is the central atom. The dihedral angle $\theta_{\angle BC/ACA}$ between the 10 ACA-plane and a line defined by a third bond with C, specifically that corresponding to a C-B-bond MO, is calculated from the bond angle $\theta_{\angle ACA}$ and the distances between the A, B, and C atoms. The distance d_1 along the bisector of $\theta_{\angle ACA}$ from C to the internuclear-distance line between A and A, $2c'_{A-A}$, is given by

$$d_{1} = 2c'_{C-A} \cos \frac{\theta_{\angle ACA}}{2} \tag{15.105}$$

15 where $2c'_{C-A}$ is the internuclear distance between A and C. The atoms A, A, and B define the base of a pyramid. Then, the pyramidal angle $\theta_{\angle ABA}$ can be solved from the internuclear distances between A and A, $2c'_{A-A}$, and between A and B, $2c'_{A-B}$, using the law of cosines (Eq. (15.98)):

$$\theta_{\angle ABA} = \cos^{-1} \left(\frac{\left(2c'_{A-B}\right)^2 + \left(2c'_{A-B}\right)^2 - \left(2c'_{A-A}\right)^2}{2\left(2c'_{A-B}\right)\left(2c'_{A-B}\right)} \right)$$
(15.106)

20 Then, the distance d_2 along the bisector of $\theta_{\angle ABA}$ from B to the internuclear-distance line $2c'_{A-A}$, is given by

$$d_2 = 2c'_{A-B}\cos\frac{\theta_{\angle ABA}}{2} \tag{15.107}$$

The lengths d_1 , d_2 , and $2c'_{C-B}$ define a triangle wherein the angle between d_1 and the internuclear distance between B and C, $2c'_{C-B}$, is the dihedral angle $\theta_{\angle BC/ACA}$ that can be solved using the law of cosines (Eq. (15.98)):

$$\theta_{\angle BC/ACA} = \cos^{-1} \left(\frac{d_1^2 + (2c'_{C-B})^2 - d_2^2}{2d_1(2c'_{B-C})} \right)$$
(15.108)

SOLUTION OF GEOMETRICAL AND ENERGY PARAMETERS OF MAJOR FUNCTIONAL GROUPS AND CORRESPONDING ORGANIC 5 MOLECULES

The exemplary molecules given in the following sections were solved using the solutions of organic chemical functional groups as basis elements wherein the structures and energies where linearly added to achieve the molecular solutions. Each functional group can be treated as a building block to form any desired molecular solution from the corresponding linear combination. Each functional group element was solved using the atomic orbital and hybrid orbital spherical orbitsphere solutions bridged by molecular orbitals comprised of the H_2 -type prolate spheroidal solution given in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. The energy of each MO was matched at the HO or AO by matching the hybridization and total energy of the MO to the AOs and HOs. The energy E_{mag} (e.g. given by Eq. (15.58)) for a $C2sp^3$ HO and Eq.(15.59) for an O2p AO) was subtracted for each set of unpaired electrons created by bond breakage.

The bond energy is not equal to the component energy of each bond as it exists in the molecule; although, they are close. The total energy of each group is its contribution to the total energy of the molecule as a whole. The determination of the bond energies for the creation of the separate parts must take into account the energy of the formation of any radicals and any redistribution of charge density within the pieces and the corresponding energy change with bond cleavage. Also, the vibrational energy in the transition state is dependent on the other groups that are bound to a given functional group. This will effect the functional-group energy. But, because the variations in the energy based on the balance of the molecular composition are typically of the order of a few hundreds of electron volts at most, they were neglected.

The energy of each functional-group MO bonding to a given carbon HO is independently matched to the HO by subtracting the contribution to the change in the energy of the HO from the total MO energy given by the sum of the MO contributions and $E(C,2sp^3) = -14.63489 \ eV$ (Eq. (13.428)). The intercept angles are determined from Eqs.

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(15.71-15.78) using the final radius of the HO of each atom. The final carbon-atom radius is determined using Eqs. (15.32) wherein the sum of the energy contributions of each atom to all the MOs in which it participates in bonding is determined. This final radius is used in Eqs. (15.19) and (15.20) to calculate the final valence energy of the HO of each atom at the corresponding final radius. The radius of any bonding heteroatom that contributes to a MO is calculated in the same manner, and the energy of its outermost shell is matched to that of the MO by the hybridization factor between the carbon-HO energy and the energy of the heteroatomic shell. The donation of electron density to the AOs and HOs reduces the energy. The donation of the electron density to the MO's at each AO or HO is that which causes the resulting energy to be divided equally between the participating AOs or HOs to achieve energy matching.

The molecular solutions can be used to design synthetic pathways and predict product yields based on equilibrium constants calculated from the heats of formation. New stable compositions of matter can be predicted as well as the structures of combinatorial chemistry reactions. Further important pharmaceutical applications include the ability to graphically or computationally render the structures of drugs that permit the identification of the biologically active parts of the molecules to be identified from the common spatial charge-density functions of a series of active molecules. Drugs can be designed according to geometrical parameters and bonding interactions with the data of the structure of the active site of the drug.

To calculate conformations, folding, and physical properties, the exact solutions of the charge distributions in any given molecule are used to calculate the fields, and from the fields, the interactions between groups of the same molecule or between groups on different molecules are calculated wherein the interactions are distance and relative orientation dependent. The fields and interactions can be determined using a finite-element-analysis approach of Maxwell's equations.

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AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple H_2 -type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule (C_6H_6) section can be generalized to any aromatic function group(s) of aromatic and heterocyclic compounds.

 C_6H_6 can be considered a linear combination of three ethylene molecules wherein a C-H bond of each CH_2 group of $H_2C=CH_2$ is replaced by a C=C bond to form a six-10 member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule (CH_2CH_2) section. The radius $r_{ethylene2sp^3}$ $(0.85252a_0)$ of the $C2sp^3$ shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy $E_{Coulomb}(C_{ethylene}, 2sp^3)$ (-15.95955 eV) of the outer electron of the $C2sp^3$ shell is given by Eq. (14.245). The energy $E\left(C_{ethylene}, 2sp^3\right)$ (-15.76868 eV) of the outer electron of the $C2sp^3$ shell 15 is given by Eq. (14.246). $E_T(C = C, 2sp^3)$ (-1.13380 eV) (Eq. (14.247), the energy change of each $C2sp^3$ shell with the formation of the C=C-bond MO is given by the difference between $E(C_{ethylene}, 2sp^3)$ and $E(C, 2sp^3)$. C_6H_6 can be solved using the same principles as those used to solve ethylene wherein the 2s and 2p shells of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two C2sp3 hybridized orbitals 20 (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each 2sp3 HO of each carbon atom initially has four unpaired electrons. Thus, the 6 H atomic orbitals (AOs) of benzene contribute six electrons and the six sp^3 -hybridized carbon atoms contribute twenty-four electrons to form six C-H bonds and six C = C bonds. Each C - H bond has two paired electrons with one donated from the H AO 25 and the other from the $C2sp^3$ HO. Each C=C bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two C2sp3 HOs of the participating carbon atoms. Each C-H and each C=C bond comprises a linear combination of one and two diatomic H_2 -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

Consider the case where three sets of C = C-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two $C2sp^3$ HOs and 75% of a H_2 -type ellipsoidal MO divided between the $C2sp^3$ HOs:

The linear combination of each H_2 -type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution per bond from each $C2sp^3$ HO to the C=C-bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond C=C-bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the C=C-bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each C = C-bond gives rise to the $C_{benzene} 2sp^3$ HO-shell Coulombic energy $E_{Coulomb} \left(C_{benzene}, 2sp^3 \right)$ given by Eq. (14.245). To meet the equipotential condition of the union of the six $C2sp^3$ HOs, c_2 and c_3 of Eq. (15.42) for the

aromatic C = C-bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of $E_{Coulomb}\left(C_{benzene}, 2sp^3\right)$ (Eq. (14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H (Eq. (1.243)):

$$C_2$$
 (benzeneC2sp³HO)= c_2 (benzeneC2sp³HO)= $\frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252$ (15.143)

The energies of each C=C bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of benzene. Ethylene serves as a basis element for the C=C bonding of benzene wherein each of the six C=C bonds of benzene comprises (0.75)(4)=3 electrons according to Eq. (15.142). The total energy of the bonds of the eighteen electrons of the C=C bonds of benzene, $E_T\left(C_6H_6,C=C\right)$, is given by (6)(0.75) times $E_{T+osc}\left(C=C\right)$ (Eq. (14.492)), the total energy of the C=C-bond MO of benzene including the Doppler term, minus eighteen times $E\left(C,2sp^3\right)$ (Eq. (14.146)), the initial energy of each $C2sp^3$ HO of each C that forms the C=C bonds of bond order two. Thus, the total energy of the six C=C bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$E_{T}\left(C_{6}H_{6},C=C\right) = (6)(0.75)E_{T+osc}\left(C=C\right) - (6)(3)E\left(C,2sp^{3}\right)$$

$$= (6)(0.75)\left(-66.05796 \ eV\right) - 18\left(-14.63489 \ eV\right)$$

$$= -297.26081 \ eV - \left(-263.42798 \ eV\right)$$

$$= -33.83284 \ eV$$
(15.144)

25 The results of benzene can be generalized to the class of aromatic and heterocyclic compounds. $E_{h\nu}$ of an aromatic bond is given by $E_T (H_2)$ (Eqs. (11.212) and (14.486)), the maximum total energy of each H_2 -type MO such that

$$\overline{E}_{osc} = n_1 \left(\overline{E}_D + \overline{E}_{Kvib} \right) = n_1 \left(-31.63536831 \ eV \sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$
 (15.145)

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two given in the Benzene Molecule (C_6H_6) section modifies Eqs. (15.52-15.56). Multiplication of

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the total energy given by Eq. (15.55) by $f_1 = 0.75$ with the substitution of Eq. (15.145) gives the total energy of the aromatic bond:

$$E_{T} \text{ (Group)} = f_{1} \left(E(basis\ energies) + E_{T} \left(atom - atom, msp^{3}.AO \right) -31.63536831\ eV \sqrt{\frac{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}{\frac{m_{e}}{m_{e}}} + n_{1}\overline{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}}} \right)$$
(15.146)

5 The total bond energy of the aromatic group E_D (Group) is the negative difference of the total energy of the group (Eq. (15.146)) and the total energy of the starting species given by the sum of $c_4 E_{initial}$ ($c_4 AO / HO$) and $c_5 E_{initial}$ ($c_5 AO / HO$):

$$E_{D}(Group) = -\begin{pmatrix} E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO) \\ -31.63536831\ eV \sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}} \\ -(c_{4}E_{initial}(AO/HO) + c_{5}E_{initial}(c_{5}AO/HO)) \end{pmatrix}$$
(15.147)

Since there are three electrons per aromatic bond, c_4 is three times the number of aromatic 10 bonds.

Benzene can also be considered as comprising chemical bonds between six CH radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of CH is given in the Hydrogen Carbide (CH) section. Those of the benzene are given in the Benzene Molecule (C_6H_6) section. The energy components of V_e , V_p ,

15 T, V_m , and E_T are the same as those of the hydrogen carbide radical, except that $E_T\left(C=C,2sp^3\right)=-1.13379~eV$ (Eq. (14.247)) is subtracted from $E_T\left(CH\right)$ of Eq. (13.495) to match the energy of each C-H-bond MO to the decrease in the energy of the corresponding $C2sp^3$ HO. In the corresponding generalization of the aromatic CH group, the geometrical parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with $E_T\left(atom-atom,msp^3.AO\right)=-1.13379~eV$.

The total energy of the benzene C-H-bond MO, $E_{T_{benzene}}\left(C-H\right)$, given by Eq. (14.467) is the sum of $0.5E_{T}\left(C=C,2sp^{3}\right)$, the energy change of each $C2sp^{3}$ shell per single bond due to the decrease in radius with the formation of the corresponding C=C-bond MO (Eq. (14.247)), and $E_{T_{benzene}}\left(CH\right)$, the σ MO contribution given by Eq. (14.441). In the corresponding generalization of the aromatic CH group, the energy parameters are determined using Eqs. (15.146-15.147) with $f_{1}=1$ and $E_{T}\left(atom-atom,msp^{3}.AO\right)=\frac{-1.13379\ eV}{2}$. Thus, the energy

contribution to the single aromatic CH bond is one half that of the C=C double bond contribution. This matches the energies of the CH and C=C aromatic groups, conserves the electron number with the equivalent charge density as that of s=1 in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic C=C bonds to give CH groups creates unpaired electrons in these fragments that corresponds to $c_3=1$ in Eq. (15.56) with E_{max} given by Eq. (15.58).

Each of the C-H bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each C-H bond, $-E_{D_{benzene}}\binom{12}{CH}$ (Eq. (14.477)), the total energy of the twelve electrons of the six C-H bonds of benzene, $E_T(C_6H_6,C-H)$, given by Eq. (14.494) 10 is

$$E_T(C_6H_6, C-H) = (6)(-E_{D_{benzene}}(^{12}CH)) = 6(-3.90454 \ eV) = -23.42724 \ eV$$
 (15.148)

The total bond dissociation energy of benzene, $E_D(C_6H_6)$, given by Eq. (14.495) is the negative

sum of
$$E_T \left(C_6 H_6, C = C \right)$$
 (Eq. (14.493)) and $E_T \left(C_6 H_6, C - H \right)$ (Eq. (14.494)):

$$E_{D}(C_{6}H_{6}) = -\left(E_{T}(C_{6}H_{6}, C = C) + E_{T}(C_{6}H_{6}, C - H)\right)$$

$$= -\left((-33.83284 \ eV) + (-23.42724 \ eV)\right)$$

$$= 57.2601 \ eV$$
(15.149)

15 Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule (C_6H_6) section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and hertocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aromatics and hertocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each E_D (Group) of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.79-15.108) are given in Table 15.218.

Table 15.213. The symbols of functional groups of aromatics and hertocyclics.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	<i>CH</i> (i)

Table 15.214. The geometrical bond parameters of aromatics and hertocyclics and

experimental values [1].

Parameter	$C \stackrel{3e}{=} C$ Group	<i>CH</i> Group
$a\left(a_{_{0}}\right)$	1.47348	1.60061
$c'(a_0)$	1.31468	1.03299
Bond Length $2c'(\Box)$	1.39140	1.09327
Exp. Bond Length	1.399 (benzene)	1.101 (benzene)
b,c (a_0)	0.66540	1.22265
e	0.89223	0.64537

5 Table 15.216. The energy parameters (eV) of functional groups of aromatics and heterocyclics.

Parameters	C = C Group	CH Group
f_1	0.75	1
n_1	2	1
n_2	0	0
n_3	0	0
C_1	0.5	0.75
C_2	0.85252	1
c_1	1	1
c_2	0.85252	0.91771
c_3	0	1
c_4	3	. 1
c_5	0	1
C_{1o}	0.5	0.75
C_{2o}	0.85252	1
V_e (eV)	-101.12679	-37.10024
V_p (eV)	20.69825	13.17125
T(eV)	34.31559	11.58941
V_m (eV)	-17.15779	-5.79470
E(AO/HO)(eV)	0	-14.63489
ΔE_{H_2MO} (AO/HO) (eV)	0	-1.13379

	T/4	
E_T (40/H0) (eV)	0	-13.50110
$E_T(H_2MO)(eV)$	-63.27075	-31.63539
E_{T} $\left(atom-atom, msp^{3}.AO\right) (eV)$	-2.26759	-0.56690
E_{T} (MO) (eV)	-65.53833	-32.20226
$\omega \left(10^{15} rad / s\right)$	49.7272	26.4826
E_{K} (eV)	32.73133	17.43132
\bar{E}_{D} (eV)	-0.35806	-0.26130
\overline{E}_{Kvib} (eV)	0.19649 [49]	0.35532 Eq. (13.458)
\bar{E}_{osc} (eV)	-0.25982	-0.08364
E_{mag} (eV)	0.14803	0.14803
$E_T(Group)(eV)$	-49.54347	-32.28590
$E_{initial}(\epsilon_4)$ AO/HO (eV)	-14.63489	-14.63489
E _{initial} (c _s AOIHO) (eV)	0	-13.59844
E_D (Group) (eV)	5.63881	3.90454

Table 15.215. The MO to HO intercept geometrical bond parameters of benzene. E_r is E_r (atom – atom, msp^3 .AO).

Bond	Atom	E_T	E_T	E_T	E_r	Final Total	Finitial	Pfinal
		(eV)	(eV)	(eV)	(eV)	Energy	(")	
		Bond 1	Bond 2	Bond 3	Bond 4	$C2sp^3$	<u></u>	(n)
						(eV)		
$\mid C-H(CH)\mid$	Ü	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597
$C = HC_a = C$	C_a	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597

Bond	E (C) (m3)(eV)	E(C1) 3)	18	А	В	K	, ,
	Contamb Cary	1 de72	٥	5~	2~	3,	z ²
	Final	(eV) Final	<u></u>	<u></u>	<u></u>	(a_o)	$(a_{\scriptscriptstyle 0})$
C-H(CH)	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C = HC_a = C$	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the experimental values [2].

	Relative Error	0.00006	
	Experimental Total Bond Energy (eV)	57.26340	
	ı	5.	
.[7]	Calculated Total Bond Energy (eV)	57.26008	
1 rapid 12:210 compand to an experiment talact	CH	9	
va am an namar	C=C	9	
TOO O TOTO TO	a Name	J ₆ H ₆ Benzene	
אד דתר	Formula	C,H,	

Table 15.218. The bond angle parameters of benzene and experimental values [1]. E_T is E_T (atom – atom, msp^3 .AO)

		
5		
C_1	~	
C_2 C_1 C_2 Atom 2	0.79232 0.79232	
C ₂ Atom 1	0.79232	
Atom 2 Hybridization Designation (Table 15.3.A)	34	
Ecoulombic Atom 2	-17.17218	
(a_0) $E_{Coulombic}$ $E_{Coulombic}$ $E_{Coulombic}$ $E_{Sybridization}$ $E_{Signation}$ $E_{Signation}$ $E_{Signation}$ $E_{Signation}$ $E_{Signation}$ $E_{Signation}$	34	
Ecoulombic Atom 1	2.62936 2.62936 4.5585 -17.17218	
$2c'$ Terminal Atoms (a_0)	4.5585	
$2c'$ Bond 2 (a_b)	2.62936	
$2c'$ Bond 1 (a_0)	2.62936	
Atoms of Angle	ZCCC (aromatic)	ZCCH (aromatic)

Atoms of Angle	<i>ა</i> ~	252	E_T	φ [*] (θ_1	9 2	Cal. θ	Exp. θ	
			(Aa)	()	(a)	<u></u>	\supset		
2007	,	0.70737	72838 1	I			01 001	120 [50-52]	
romatic)	7	0.17454	1.0000				120.19	(penzene)	
НЭЭ7					01 001		110.01	120 [50-52]	
aromatic)			-	,	120.19		119.91	(benzene)	

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Table 1.1. The calculated and experimental total bond energies of n-alkanes using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
C_3H_8	Propane	41.46896	41.434	-0.00085
C_4H_{10}	Butane	53.62666	53.61	-0.00036
C_5H_{12}	Pentane	65.78436	65.77	-0.00017
C_6H_{14}	Hexane	77.94206	77.93	-0.00019
C_7H_{16}	Heptane	90.09976	90.09	-0.00013
C_8H_{18}	Octane	102.25746	102.25	-0.00006
C_9H_{20}	Nonane	114,41516	114.40	-0.00012
$C_{10}H_{22}$	Decane	126.57286	126.57	-0.00003
$C_{11}H_{24}$	Undecane	138.73056	138.736	0.00004
$C_{12}H_{26}$	Dodecane	150.88826	150.88	-0.00008
$C_{18}H_{38}$	Octadecane	223.83446	223.85	0.00008

Table 1.2. The calculated and experimental total bond energies of branched alkanes using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Erro
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
C_4H_{10}	Isobutane	53.69922	53.695	-0.00007
C_5H_{12}	Isopentane	65.85692	65.843	-0.00021
C_5H_{12}	Neopentane	65.86336	65.992	0.00195
C_6H_{14}	2-Methylpentane	78.01462	78.007	-0.00010
C_6H_{14}	3-Methylpentane	78.01462	77.979	-0.00046
C_6H_{14}	2,2-Dimethylbutane	78.02106	78.124	0.00132
C_6H_{14}	2,3-Dimethylbutane	77.99581	78.043	0.00061
C_7H_{16}	2-Methylhexane	90.17232	90.160	-0.00014
C_7H_{16}	3-Methylhexane	90.17232	90.127	-0.00051
C_7H_{16}	3-Ethylpentane	90.17232	90.108	-0.00072
C ₇ H ₁₆	2,2-Dimethylpentane	90.17876	90.276	0.00107
C_7H_{16}	2,2,3-Trimethylbutane	90.22301	90.262	0.00044
C ₇ H ₁₆	2,4-Dimethylpentane	90.24488	90.233	-0.00013
C_7H_{16}	3,3-Dimethylpentane	90.17876	90.227	0.00054
C_8H_{18}	2-Methylheptane	102.33002	102.322	-0.00008
C_8H_{18}	3-Methylheptane	102.33002	102.293	-0.00036
C_8H_{18}	4-Methylheptane	102.33002	102.286	-0.00043
C_8H_{18}	3-Ethylhexane	102.30169	102.274	-0.00027
C_8H_{18}	2,2-Dimethylhexane	102.33646	102.417	0.00079
C_8H_{18}	2,3-Dimethylhexane	102.31121	102.306	-0.00005
C_8H_{18}	2,4-Dimethylhexane	102.40258	102.362	-0.00040
C ₈ H ₁₈	2,5-Dimethylhexane	102.40258	102.396	-0.00006
C_8H_{18}	3,3-Dimethylhexane	102.33646	102.369	0.00032
C ₈ H ₁₈	3,4-Dimethylhexane	102.31121	102.296	-0.00015
C_8H_{18}	3-Ethyl-2-methylpentane	102.31121	102.277	-0.00033
C ₈ H ₁₈	3-Ethyl-3-methylpentane	102.33646	102.317	-0.00019
C ₈ H ₁₈	2,2,3-Trimethylpentane	102.38071	102.370	-0.00010
C_8H_{18}	2,2,4-Trimethylpentane	102.40902	102.412	0.00003
C ₈ H ₁₈	2,3,3-Trimethylpentane	102.38071	102.332	-0.00048
C_8H_{18}	2,3,4-Trimethylpentane	102.29240	102.342	0.00049
C ₈ H ₁₈	2,2,3,3-Tetramethylbutane	102.41632	102.433	0.00016
C ₉ H ₂₀	2,3,5-Trimethylhexane	114.54147	114.551	0.00008
C ₉ H ₂₀	3,3-Diethylpentane	114.49416	114.455	-0.00034
C ₉ H ₂₀	2,2,3,3-Tetramethylpentane	114.57402	114.494	-0.00070
C ₉ H ₂₀	2,2,3,4-Tetramethylpentane	114.51960	114.492	-0.00024

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₉ H ₂₀	2,2,4,4-Tetramethylpentane	114.57316	114.541	-0.00028
C_9H_{20}	2,3,3,4-Tetramethylpentane	114.58266	114.484	-0.00086
$C_{10}H_{22}$	2-Methylnonane	126.64542	126.680	0.00027
$C_{10}H_{22}$	5-Methylnonane	126.64542	126.663	0.00014

Table 1.3. The calculated and experimental total bond energies of alkenes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_6	Propene	35.56033	35.63207	0.00201
$C_{3}H_{6}$ $C_{4}H_{8}$	1-Butene	47.71803	47.78477	0.00140
C_4H_8	trans-2-Butene	47.93116	47.90395	-0.00057
C_4H_8	Isobutene	47.90314	47.96096	0.00121
C_5H_{10}	1-Pentene	59.87573	59.95094	0.00121
C_5H_{10}	trans-2-Pentene	60.08886	60.06287	-0.00043
C_5H_{10}	2-Methyl-1-butene	60.06084	60.09707	0.00043
	2-Methyl-2-butene	60.21433	60.16444	-0.00083
C_5H_{10}	3-Methyl-1-butene	59.97662	60.01727	0.00068
C_5H_{10}	1-Hexene	72.03343	72.12954	0.0003
C_6H_{12}	trans-2-Hexene	72.24656	72.12934	-0.00013
C_6H_{12}		72.24656	72.24251	-0.00013
C_6H_{12}	trans-3-Hexene	72.24636 72.21854	72.29433	0.00105
C_6H_{12}	2-Methyl-1-pentene			
C_6H_{12}	2-Methyl-2-pentene	72.37203	72.37206	0.00000
C_6H_{12}	3-Methyl-1-pentene	72.13432	72.19173	0.00080
C_6H_{12}	4-Methyl-1-pentene	72.10599	72.21038	0.00145
C_6H_{12}	3-Methyl-trans-2-pentene	72.37203	72.33268	-0.00054
C_6H_{12}	4-Methyl-trans-2-pentene	72.34745	72.31610	-0.00043
C_6H_{12}	2-Ethyl-1-butene	72.21854	72.25909	0.00056
C_6H_{12}	2,3-Dimethyl-1-butene	72.31943	72.32543	0.00008
C_6H_{12}	3,3-Dimethyl-1-butene	72.31796	72.30366	-0.00020
C_6H_{12}	2,3-Dimethyl-2-butene	72.49750	72.38450	-0.00156
C_7H_{14}	1-Heptene	84.19113	84.27084	0.00095
C_7H_{14}	5-Methyl-1-hexene	84.26369	84.30608	0.00050
C_7H_{14}	trans-3-Methyl-3-hexene	84.52973	84.42112	-0.00129
C_7H_{14}	2,4-Dimethyl-1-pentene	84.44880	84.49367	0.00053
C_7H_{14}	4,4-Dimethyl-1-pentene	84.27012	84.47087	0.00238
C_7H_{14}	2,4-Dimethyl-2-pentene	84.63062	84.54445	-0.00102
C_7H_{14}	trans-4,4-Dimethyl-2-pentene	84.54076	84.54549	0.00006
C_7H_{14}	2-Ethyl-3-methyl-1-butene	84.47713	84.44910	-0.00033
C_7H_{14}	2,3,3-Trimethyl-1-butene	84.51274	84.51129	-0.00002
C_8H_{16}	1-Octene	96.34883	96.41421	0.00068
C_8H_{16}	trans-2,2-Dimethyl-3-hexene	96.69846	96.68782	-0.00011
C_8H_{16}	3-Ethyl-2-methyl-1-pentene	96.63483	96.61113	-0.00025
C ₈ H ₁₆	2,4,4-Trimethyl-1-pentene	96.61293	96.71684	0.00107
C ₈ H ₁₆	2,4,4-Trimethyl-2-pentene	96.67590	96.65880	-0.00018
$C_{10}H_{20}$	1-Decene	120.66423	120.74240	0.00065
$C_{12}H_{24}$	1-Dodecene	144.97963	145.07163	0.00063
$C_{16}H_{32}$	1-Hexadecene	193.61043	193.71766	0.00055

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Table 1.4. The calculated and experimental total bond energies of alkynes using closed-form equations having integers and fundamental constants only.

		*		
Formula	Name	Calculated Total Bond	Experimental Total Bond	Relative Error
		Energy (eV)	Energy (eV)	
C_3H_4	Propyne	29.42932	29,40432	-0.00085
C_4H_6	1-Butyne	41.58702	41.55495	-0.00077
C_4H_6	2-Butyne	41.72765	41,75705	0.00077
C_9H_{16}	1-Nonyne	102.37552	102,35367	-0.00070

Table 1.5. The calculated and experimental total bond energies of alkyl fluorides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CF ₄	Tetrafluoromethane	21.07992	21.016	-0.00303
CHF ₃	Trifluoromethane	19.28398	19.362	0.00405
CH_2F_2	Difluoromethane	18.22209	18.280	0.00314
C_3H_7F	1-Fluoropropane	41.86745	41.885	0.00041
C_3H_7F	2-Fluoropropane	41.96834	41.963	-0.00012

Table 1.6. The calculated and experimental total bond energies of alkyl chlorides using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
CCl_4	Tetrachloromethane	13.43181	13.448	0.00123
CHCl₃	Trichloromethane	14.49146	14.523	0.00217
CH_2Cl_2	Dichloromethane	15.37248	15.450	0.00499
CH₃Cl	Chloromethane	16.26302	16.312	0.00299
C_2H_5Cl	Chloroethane	28.61064	28.571	-0.00138
C₃H₁Cl	1-Chloropropane	40.76834	40.723	-0.00112
C ₃ H ₇ Cl	2-Chloropropane	40.86923	40.858	-0.00028
C ₄ H ₉ Cl	1-Chlorobutane	52.92604	52.903	-0.00044
C ₄ H ₉ Cl	2-Chlorobutane	53.02693	52.972	-0.00104
C ₄ H ₉ Cl	1-Chloro-2-methylpropane	52.99860	52.953	-0.00085
C ₄ H ₉ Cl	2-Chloro-2-methylpropane	53.21057	53.191	-0.00037
$C_5H_{11}Cl$	1-Chloropentane	65.08374	65.061	-0.00034
$C_5H_{11}Cl$	1-Chloro-3-methylbutane	65.15630	65.111	-0.00069
$C_5H_{11}Cl$	2-Chloro-2-methylbutane	65.36827	65,344	-0.00037
C ₅ H ₁₁ Cl	2-Chloro-3-methylbutane	65.16582	65.167	0.00002
$C_6H_{13}Cl$	2-Chlorohexane	77.34233	77.313	-0.00038
$C_8H_{17}Cl$	1-Chlorooctane	101.55684	101.564	0.00007
$C_{12}H_{25}Cl$	1-Chlorododecane	150.18764	150.202	0.00007
$C_{18}H_{37}CI$	1-Chlorooctadecane	223.13384	223.175	0.00018

Table 1.7. The calculated and experimental total bond energies of alkyl bromides using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
CBr ₄	Tetrabromomethane	11.25929	11.196	-0.00566
CHBr₃	Tribromomethane	12.87698	12.919	0.00323
CH₃Br	Bromomethane	15.67551	15.732	0.00360
C_2H_5Br	Bromoethane	28.03939	27.953	-0.00308
C_3H_7Br	1-Bromopropane	40.19709	40.160	-0.00093
C ₃ H ₇ Br	2-Bromopropane	40.29798	40.288	-0.00024
$C_5H_{10}Br_2$	2,3-Dibromo-2-methylbutane	63.48143	63.477	-0.00007
$C_6H_{13}Br$	1-Bromohexane	76.67019	76.634	-0.00047
$C_7H_{15}Br$	1-Bromoheptane	88.82789	88.783	-0.00051
$C_8H_{17}Br$	1-Bromooctane	100.98559	100.952	-0.00033
$C_{12}H_{25}Br$	1-Bromododecane	149.61639	149.573	-0.00029
$C_{16}H_{33}Br$	1-Bromohexadecane	198.24719	198.192	-0.00028

Table 1.8. The calculated and experimental total bond energies of alkyl iodides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CHI ₃	Triiodomethane	10.35888	10.405	0.00444
CH_2I_2	Diiodomethane	12.94614	12.921	-0.00195
CH₃I	Iodomethane	15.20294	15.163	-0.00263
C_2H_5I	Iodoethane	27.36064	27.343	-0.00066
C_3H_7I	1-Iodopropane	39.51834	39.516	-0.00006
C_3H_7I	2-Iodopropane	39.61923	39.623	0.00009
C ₄ H ₉ I	2-Iodo-2-methylpropane	51.96057	51.899	-0.00119

Table 1.9. The calculated and experimental total bond energies of alkene halides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond	Experimental Total Bond	Relative Error
C ₂ H ₃ Cl	Chloroethene	Energy (eV) 22.46700	Energy (eV) 22.505	0.00170
C ₃ H ₅ Cl	2-Chloropropene	35.02984	35.05482	0.00071

Table 1.10. The calculated and experimental total bond energies of alcohols using closed-form equations having integers and fundamental constants only.

				
		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
CH ₄ O	Methanol	21.11038	21.131	0.00097
C_2H_6O	Ethanol	33.40563	33.428	0.00066
C₃H ₈ O	1-Propanol	45.56333	45.584	0.00046
C_3H_8O	2-Propanol	45.72088	45.766	0.00098
$C_4H_{10}O$	1-Butanol	57.72103	57.736	0.00026
$C_4H_{10}O$	2-Butanol	57.87858	57.922	0.00074
$C_4H_{10}O$	2-Methyl-1-propananol	57.79359	57.828	0.00060
$C_4H_{10}O$	2-Methyl-2-propananol	58.15359	58.126	-0.00048
$C_5H_{12}O$	1-Pentanol	69.87873	69.887	0.00011

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)_	
C ₅ H ₁₂ O	2-Pentanol	70.03628	70.057	0.00029
$C_5H_{12}O$	3-Pentanol	70.03628	70.097	0.00087
$C_5H_{12}O$	2-Methyl-1-butananol	69.95129	69.957	80000.0
$C_5H_{12}O$	3-Methyl-1-butananol	69.95129	69.950	-0.00002
$C_5H_{12}O$	2-Methyl-2-butananol	70.31129	70.246	-0.00092
$C_5H_{12}O$	3-Methyl-2-butananol	69.96081	70.083	0.00174
$C_6H_{14}O$	1-Hexanol	82.03643	82.054	0.00021
$C_6H_{14}O$	2-Hexanol	82.19398	82.236	0.00052
$C_7H_{16}O$	1-Heptanol	94.19413	94.214	0.00021
$C_8H_{18}O$	1-Octanol	106.35183	106.358	0.00006
$C_8H_{18}O$	2-Ethyl-1-hexananol	106.42439	106.459	0.00032
$C_9H_{20}O$	1-Nonanol	118.50953	118.521	0.00010
$C_{10}H_{22}O$	1-Decanol	130.66723	130.676	0.00007
$C_{12}H_{26}O$	1-Dodecanol	154.98263	154.984	0.00001
$C_{16}H_{34}O$	1-Hexadecanol	203.61343	203.603	-0.00005

Table 1.11. The calculated and experimental total bond energies of ethers using closed-form equations having integers and fundamental constants only.

	*	Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
,	W	Energy (eV)	Energy (eV)	
C ₂ H ₆ O	Dimethyl ether	32.84496	32.902	0.00174
C_3H_8O	Ethyl methyl ether	45.19710	45.183	-0.00030
$C_4H_{10}O$	Diethyl ether	57.54924	57.500	-0.00086
$C_4H_{10}O$	Methyl propyl ether	57.35480	57.355	0.00000
$C_4H_{10}O$	Isopropyl methyl ether	57.45569	57.499	0.00075
$C_6H_{14}O$	Dipropyl ether	81.86464	81.817	-0.00059
$C_6H_{14}O$	Disopropyl ether	82.06642	82.088	0.00026
$C_6H_{14}O$	t-Butyl ethyl ether	82.10276	82.033	-0.00085
$C_7H_{16}O$	t-Butyl isopropyl ether	94.36135	94.438	0.00081
$C_8H_{18}O$	Dibutyl ether	106.18004	106.122	-0.00055
$C_8H_{18}O$	Di-sec-butyl ether	106.38182	106.410	0.00027
$C_8H_{18}O$	Di-t-butyl ether	106.36022	106.425	0.00061
$C_8H_{18}O$	t-Butyl isobutyl ether	106.65628	106.497	-0.00218

Table 1.12. The calculated and experimental total bond energies of 1° amines using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
CH₅N	Methylamine	23.88297	23.857	-0.00110
C_2H_7N	Ethylamine	36.04067	36.062	0.00060
C_3H_9N	Propylamine	48.19837	48.243	0.00092
$C_4H_{11}N$	Butylamine	60.35607	60.415	0.00098
$C_4H_{11}N$	sec-Butylamine	60.45696	60.547	0.00148
$C_4H_{11}N$	t-Butylamine	60.78863	60.717	-0.00118
$C_4H_{11}N$	Isobutylamine	60.42863	60.486	0.00094

Table 1.13. The calculated and experimental total bond energies of 2° amines using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
C ₂ H ₇ N	Dimethylamine	35.76895	35.765	-0.00012
$C_4H_{11}N$	Diethylamine	60.22930	60.211	-0.00030
$C_6H_{15}N$	Dipropylamine	84.54470	84.558	0.00016
$C_6H_{15}N$	Diisopropylamine	84.74648	84.846	0.00117
$C_8H_{19}N$	Dibutylamine	108.86010	108.872	0.00011
$C_8H_{19}N$	Diisobutylamine	109.00522	109.106	0.00092

Table 1.14. The calculated and experimental total bond energies of 3° amines using closed-form equations having integers and fundamental constants only.

	Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
_	C ₃ H ₉ N	Trimethylamine	47.83338	47.761	-0.00152
	$C_6H_{15}N$	Triethylamine	84.30648	84.316	0.00012
	$C_9H_{21}N$	Tripropylamine	120.77958	120.864	0.00070

Table 1.15. The calculated and experimental total bond energies of aldehydes using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	2 -
		Energy (eV)_	Energy (eV)	7
CH ₂ O	Formaldehyde	15.64628	15.655	0.00056
C_2H_4O	Acetaldehyde	28.18711	28.198	0.00039
C_3H_6O	Propanal	40.34481	40.345	0.00000
C_4H_8O	Butanal	52.50251	52.491	-0.00022
C ₄ H ₈ O	Isobutanal	52.60340	52.604	0.00001
$C_5H_{10}O$	Pentanal	64.66021	64.682	0.00034
$C_7H_{14}O$	Heptanal	88.97561	88.942	-0.00038
$C_8H_{16}O$	Octanal	101.13331	101.179	0.00045
$C_8H_{16}O$	2-Ethylhexanal	101.20587	101.259	0.00053

Table 1.16. The calculated and experimental total bond energies of ketones using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
C ₃ H ₆ O	Acetone	40.68472	40.672	-0.00031
C_4H_8O	2-Butanone	52.84242	52.84	-0.00005
$C_5H_{10}O$	2-Pentanone	65.00012	64.997	-0.00005
$C_5H_{10}O$	3-Pentanone	65.00012	64.997	-0.00005
$C_5H_{10}O$	3-Methyl-2-butanone	65.10101	65.036	-0.00099
$C_6H_{12}O$	2-Hexanone	77.15782	77.152	-0.00008
$C_6H_{12}O$	3-Hexanone	77.15782	77.138	-0.00025
$C_6H_{12}O$	2-Methyl-3-pentanone	77.25871	77.225	-0.00043
$C_6H_{12}O$	3,3-Dimethyl-2-butanone	77.29432	77.273	-0.00028
$C_7H_{14}O$	3-Heptanone	89.31552	89.287	-0.00032
$C_7H_{14}O$	4-Heptanone	89.31552	89.299	-0.00018
$C_7H_{14}O$	2,2-Dimethyl-3-pentanone	89.45202	89.458	0.00007

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		Calculated	Experimental	Relative Error	
Formula	Name	Total Bond	Total Bond		
		Energy (eV)	Energy (eV)		
$C_7H_{14}O$	2,4-Dimethyl-3-pentanone	89.51730	89.434	-0.00093	
$C_8H_{16}O$	2,2,4-Trimethyl-3-pentanone	101.71061	101.660	-0.00049	
$C_9H_{18}O$	2-Nonanone	113.63092	113.632	0.00001	
$C_9H_{18}O$	5-Nonanone	113.63092	113.675	0.00039	
$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	113.77604	113.807	0.00027	

Table 1.17. The calculated and experimental total bond energies of carboxylic acids using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH ₂ O ₂	Formic acid	21.01945	21.036	0.00079
$C_2H_4O_2$	Acetic acid	33.55916	33.537	-0.00066
$C_3H_6O_2$	Propanoic acid	45.71686	45.727	0.00022
$C_4H_8O_2$	Butanoic acid	57.87456	57.883	0.00015
$C_5H_{10}O_2$	Pentanoic acid	70.03226	69.995	-0.00053
$C_5H_{10}O_2$	3-Methylbutanoic acid	70.10482	70.183	0.00111
$C_5H_{10}O_2$	2,2-Dimethylpropanoic acid	70.31679	69.989	-0.00468
$C_6H_{12}O_2$	Hexanoic acid	82.18996	82.149	-0.00050
$C_7H_{14}O_2$	Heptanoic acid	94.34766	94.347	0.00000
$C_8H_{16}O_2$	Octanoic acid	106.50536	106.481	-0.00022
$C_9H_{18}O_2$	Nonanoic acid	118.66306	118.666	0.00003
$C_{10}H_{20}O_2$	Decanoic acid	130.82076	130.795	-0.00020
$C_{12}H_{24}O_2$	Dodecanoic acid	155.13616	155.176	0.00026
$C_{14}H_{28}O_2$	Tetradecanoic acid	179.45156	179.605	0.00085
$C_{15}H_{30}O_2$	Pentadecanoic acid	191.60926	191.606	-0.00002
$C_{16}H_{32}O_2$	Hexadecanoic acid	203.76696	203.948	0.00089
$C_{18}H_{36}O_2$	Stearic acid	228.08236	228.298	0.00094
$C_{20}H_{40}O_2$	Eicosanoic acid	252.39776	252.514	0.00046

Table 1.18. The calculated and experimental total bond energies of carboxylic acid esters using closed-form equations having integers and fundamental constants only.

			Calculated	Experimental	Relative Erro
Formula	Name		Total Bond	Total Bond	1
		- 10	Energy (eV)	Energy (eV)	·
$C_2H_4O_2$	Methyl formate		32.71076	32.762	0.00156
$C_3H_6O_2$	Methyl acetate		45.24849	45.288	0.00087
$C_6H_{12}O_2$	Methyl pentanoate		81.72159	81.726	0.00005
$C_7H_{14}O_2$	Methyl hexanoate		93.87929	93.891	0.00012
$C_8H_{16}O_2$	Methyl heptanoate		106.03699	106.079	0.00040
$C_9H_{18}O_2$	Methyl octanoate		118.19469	118.217	0.00018
$C_{10}H_{20}O_2$	Methyl nonanoate		130.35239	130.373	0.00016
$C_{11}H_{22}O_2$	Methyl decanoate		142.51009	142.523	0.00009
$C_{12}H_{24}O_2$	Methyl undecanoate		154.66779	154.677	0.00006
$C_{13}H_{26}O_2$	Methyl dodecanoate		166.82549	166.842	0.00010
$C_{14}H_{28}O_2$	Methyl tridecanoate		178.98319	179.000	0.00009
$C_{15}H_{30}O_2$	Methyl tetradecanoate		191.14089	191.170	0.00015
$C_{16}H_{32}O_2$	Methyl pentadecanoate		203.29859	203.356	0.00028
$C_4H_8O_2$	Propyl formate		57.76366	57.746	-0.00030
$C_4H_8O_2$	Ethyl acetate		57.63888	57.548	-0.00157
$C_5H_{10}O_2$	Isopropyl acetate		69.89747	69.889	-0.00013
$C_5H_{10}O_2$	Ethyl propanoate		69.79658	69.700	-0.00139
$C_6H_{12}O_2$	Butyl acetate		81.95428	81.873	-0.00099
$C_6H_{12}O_2$	t-Butyl acetate		82.23881	82.197	-0.00051

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		Calculated	Experimental	Relative Error	
Formula	Name	Total Bond	Total Bond		
		Energy (eV)	Energy (eV)		
$C_6H_{12}O_2$	Methyl 2,2-dimethylpropanoate	82.00612	81.935	-0.00087	
$C_7H_{14}O_2$	Ethyl pentanoate	94.11198	94.033	-0.00084	
$C_7H_{14}O_2$	Ethyl 3-methylbutanoate	94.18454	94.252	0.00072	
$C_7H_{14}O_2$	Ethyl 2,2-dimethylpropanoate	94.39651	94.345	-0.00054	
$C_8H_{16}O_2$	Isobutyl isobutanoate	106.44313	106.363	-0.00075	
$C_8H_{16}O_2$	Propyl pentanoate	106.26968	106.267	-0.00003	
$C_8H_{16}O_2$	Isopropyl pentanoate	106.37057	106.384	0.00013	
$C_9H_{18}O_2$	Butyl pentanoate	118.42738	118.489	0.00052	
$C_9H_{18}O_2$	sec-Butyl pentanoate	118.52827	118.624	0.00081	
$C_9H_{18}O_2$	Isobutyl pentanoate	118.49994	118.576	0.00064	

Table 1.19. The calculated and experimental total bond energies of amides using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
	w	Energy (eV)	Energy (eV)	
CH ₃ NO	Formamide	23.68712	23.697	0.00041
C ₂ H ₅ NO	Acetamide	36.15222	36.103	-0.00135
C ₃ H ₇ NO	Propanamide	48.30992	48.264	-0.00094
C ₄ H ₉ NO	Butanamide	60.46762	60.449	-0.00030
C ₄ H ₉ NO	2-Methylpropanamide	60.51509	60.455	-0.00099
C ₅ H ₁₁ NO	Pentanamide	72.62532	72.481	-0.00200
$C_5H_{11}NO$	2,2-Dimethylpropanamide	72.67890	72.718	0.00054
$C_6H_{13}NO$	Hexanamide	84.78302	84.780	-0.00004
C ₈ H ₁₇ NO	Octanamide	109.09842	109.071	-0.00025

Table 1.20. The calculated and experimental total bond energies of N-alkyl and N,N-dialkyl amides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₃ H ₇ NO	N,N-Dimethylformamide	47.53142	47.574	0.00090
C ₄ H ₉ NO	N,N-Dimethylacetamide	59.91404	59.890	-0.00041
C ₆ H ₁₃ NO	N-Butylacetamide	84.63649	84.590	-0.00055

Table 1.21. The calculated and experimental total bond energies of urea using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH ₄ N ₂ O U	Jrea	31.35919	31.393	0.00108

Table 1.22. The calculated and experimental total bond energies of acid halide using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₂ H ₃ ClO	Acetyl chloride	28.02174	27.990	-0.00115

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Table 1.23. The calculated and experimental total bond energies of acid anhydrides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₄ H ₆ O ₃	Acetic anhydride	56.94096	56.948	0.00013
$C_6H_{10}O_3$	Propanoic anhydride	81.25636	81.401	0.00177

Table 1.24. The calculated and experimental total bond energies of nitriles using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
C ₂ H ₃ N	Acetonitrile	25.72060	25.77	0.00174
C_3H_5N	Propanenitrile '	37.87830	37.94	0.00171
C_4H_7N	Butanenitrile	50,03600	50.08	0.00082
C_4H_7N	2-Methylpropanenitrile	50.13689	50.18	0.00092
C ₅ H ₉ N	Pentanenitrile	62.19370	62.26	0.00111
C_5H_9N	2,2-Dimethylpropanenitrile	62.47823	62.40	-0.00132
$C_7H_{13}N$	Heptanenitrile	86.50910	86.59	0.00089
$C_8H_{15}N$	Octanenitrile	98.66680	98.73	0.00069
$C_{10}H_{19}N$	Decanenitrile	122.98220	123.05	0.00057
$C_{14}H_{27}N$	Tetradecanenitrile	171.61300	171.70	0.00052

Table 1.25. The calculated and experimental total bond energies of thiols using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
HS	Hydrogen Sulfide	3.77430	3.653	-0.03320
H_2S	Dihydrogen Sulfide	7.56058	7.605	0.00582
CH ₄ S	Methanethiol	19.60264	19.575	-0.00141
C_2H_6S	Ethanethiol	31.76034	31.762	0.00005
C_3H_8S	1-Propanethiol	43.91804	43.933	0.00035
C_3H_8S	2-Propanethiol	44.01893	44.020	0.00003
$C_4H_{10}S$	1-Butanethiol	56.07574	56.089	0.00024
$C_4H_{10}S$	2-Butanethiol	56.17663	56.181	0.00009
$C_4H_{10}S$	2-Methyl-1-propanethiol	56.14830	56.186	0.00066
$C_4H_{10}S$	2-Methyl-2-propanethiol	56.36027	56.313	-0.00084
$C_5H_{12}S$	2-Methyl-1-butanethiol	68.30600	68.314	0.00012
$C_5H_{12}S$	1-Pentanethiol	68.23344	68.264	0.00044
$C_5H_{12}S$	2-Methyl-2-butanethiol	68.51797	68.441	-0.00113
$C_5H_{12}S$	3-Methyl-2-butanethiol	68.31552	68.381	0.00095
$C_5H_{12}S$	2,2-Dimethyl-1-propanethiol	68.51797	68.461	-0.00084
$C_6H_{14}S$	1-Hexanethiol	80.39114	80.416	0.00031
$C_6H_{14}S$	2-Methyl-2-pentanethiol	80.67567	80.607	-0.00085
$C_6H_{14}S$	2,3-Dimethyl-2-butanethiol	80.71992	80.603	-0.00145
$C_7H_{16}S$	1-Heptanethiol	92.54884	92.570	0.00023
C ₁₀ H ₂₂ S	1-Decanethiol	129.02194	129.048	0.00020

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Table 1.26. The calculated and experimental total bond energies of sulfides using closed-form equations having integers and fundamental constants only.

T21 -		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
C_2H_6S	Dimethyl sulfide	31.65668	31.672	0.00048
C_3H_8S	Ethyl methyl sulfide	43.81438	43.848	0.00078
$C_4H_{10}S$	Diethyl sulfide	55.97208	56.043	0.00126
$C_4H_{10}S$	Methyl propyl sulfide	55.97208	56.029	0.00102
$C_4H_{10}S$	Isopropyl methyl sulfide	56.07297	56.115	0.00075
$C_5H_{12}S$	Butyl methyl sulfide	68.12978	68.185	0.00081
$C_5H_{12}S$	t-Butyl methyl sulfide	68.28245	68.381	0.00144
$C_5H_{12}S$	Ethyl propyl sulfide	68.12978	68.210	0.00117
$C_5H_{12}S$	Ethyl isopropyl sulfide	68.23067	68.350	0.00174
$C_6H_{14}S$	Diisopropyl sulfide	80.48926	80.542	0.00065
$C_6H_{14}S$	Butyl ethyl sulfide	80.28748	80.395	0.00133
$C_6H_{14}S$	Methyl pentyl sulfide	80.28748	80.332	0.00056
$C_8H_{18}S$	Dibutyl sulfide	104.60288	104.701	0.00094
$C_8H_{18}S$	Di-sec-butyl sulfide	104.80466	104.701	-0.00099
$C_8H_{18}S$	Di-t-butyl sulfide	104.90822	104.920	0.00011
$C_8H_{18}S$	Diisobutyl sulfide	104.74800	104.834	0.00082
$C_{10}H_{22}S$	Ethyl propyl sulfide	128.91828	128.979	0.00047
$C_{10}H_{22}S$	Diisopentyl sulfide	129.06340	129.151	0.00068

Table 1.27. The calculated and experimental total bond energies of disulfides using closed-form equations having integers and fundamental constants only.

D 1		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
$C_2H_6S_2$	Dimethyl disulfide	34.48127	34.413	-0.00199
$C_4H_{10}S_2$	Diethyl disulfide	58.79667	58.873	0.00129
$C_6H_{14}S_2$	Dipropyl disulfide	83.11207	83.169	0.00068
$C_8H_{18}S_2$	Di-t-butyl disulfide	107.99653	107.919	-0.00072

Table 1.28. The calculated and experimental total bond energies of sulfoxides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₂ H ₆ SO	Dimethyl sulfoxide	35.52450	35.435	-0.00253
C ₄ H ₁₀ SO	Diethyl sulfoxide	59.83990	59.891	0.00085
C ₆ H ₁₄ SO	Dipropyl sulfoxide	84.15530	84.294	0.00165

Table 1.29. The calculated and experimental total bond energies of sulfones using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6SO_2$	Dimethyl sulfone	40.27588	40.316	0.00100

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Table 1.30. The calculated and experimental total bond energies of sulfites using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₂ H ₆ SO ₃ C ₄ H ₁₀ SO ₃	Dimethyl sulfite Diethyl sulfite	43.95058 68.54939	44.042 68.648	0.00207 0.00143
$C_8H_{18}SO_3$	Dibutyl sulfite	117.18019	117.191	0.00143

Table 1.31. The calculated and experimental total bond energies of sulfates using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6SO_4 \ C_4H_{10}SO_4 \ C_6H_{14}SO_4$	Dimethyl sulfate	48.70617	48.734	0.00058
	Diethyl sulfate	73.30077	73.346	0.00061
	Dipropyl sulfate	97.61617	97.609	-0.00008

Table 1.32. The calculated and experimental total bond energies of nitro alkanes using closed-form equations having integers and fundamental constants only.

,		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
CH_3NO_2	Nitromethane	25.14934	25.107	-0.00168
$C_2H_5NO_2$	Nitroethane	37.30704	37.292	-0.00040
$C_3H_7NO_2$	1-Nitropropane	49.46474	49.451	-0.00028
C₃H ₇ NO ₂	2-Nitropropane	49,56563	49.602	0.00074
$C_4H_9NO_2$	1-Nitrobutane	61.62244	61.601	-0.00036
C ₄ H ₉ NO ₂	2-Nitroisobutane	61.90697	61.945	0.00061
$C_5H_{11}NO_2$	1-Nitropentane	73.78014	73,759	-0.00028

Table 1.33. The calculated and experimental total bond energies of nitrite using closed-form equations having integers and fundamental constants only.

Formula	Name	 Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH ₃ NO ₂	Methyl nitrite	24.92328	24.955	0.00126

Table 1.34. The calculated and experimental total bond energies of nitrate using closed-form equations having integers and fundamental constants only.

	T T			
Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH ₃ NO ₃	Methyl nitrate	28.18536	28.117	-0.00244
$C_2H_5NO_3$	Ethyl nitrate	40.34306	40.396	0.00131
$C_3H_7NO_3$	Propyl nitrate	52.50076	52.550	0.00131
C ₃ H ₇ NO ₃	Isopropyl nitrate	52.60165	52.725	0.00093

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Table 1.35. The calculated and experimental total bond energies of conjugated alkenes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₅ H ₈	Cyclopentene	54.83565	54.86117	0.00047
C_4H_6	1,3 Butadiene	42.09159	42.12705	0.00047
C₅H ₈	1,3 Pentadiene	54.40776	54,42484	0.00034
C ₅ H ₈	1,4 Pentadiene	54.03745	54.11806	0.00149
C_5H_6	1,3 Cyclopentadiene	49.27432	49.30294	0.00058

Table 1.36. The calculated and experimental total bond energies of aromatics and heterocyclic aromatics using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond	Experimental Total Bond	Relative Error
		57.26008	57.26340	0.00006
C ₆ H ₅ Cl	Chlorobenzene	56.55263	56.581	0.00051
C ₆ H ₄ Cl ₂	m-dichlorobenzene	55.84518	55.852	0.00012
C ₆ H ₃ Cl ₃	1,2,3-trichlorobenzene	55.13773	55.077	-0.00111
C ₆ H ₃ Cl ₃	1,3,5-trichlorbenzene	55.29542	55.255	-0.00073
C ₆ Cl ₆	Hexachlorobenzene	52.57130	52.477	-0.00179
C ₆ H ₅ NO ₂	Nitrobenzene	65.18754	65.217	0.00046
C_7H_8	Toluene	69.48425	69.546	0.00088
$C_7H_6O_2$	Benzoic acid	73.76938	73.762	-0.00009
C ₇ H ₅ ClO ₂	2-chlorobenzoic acid	73.06193	73.082	0.00027
$C_7H_5ClO_2$	3-chlorobenzoic acid	73.26820	73.261	-0.00010
C ₇ H ₅ ClO ₂	4-chlorobenzoic acid	73.26820	73.247	-0.00028
C_6H_7N	Aniline	64.43373	64.374	-0.00093
C_7H_9N	2-methylaniline	76.62345	76.643	-0.00025
C_7H_9N	3-methylaniline	76.62345	76.661	0.00050
C_7H_9N	4-methylaniline	76.62345	76.654	0.00040
$C_6H_6N_2O_2$	2-nitroaniline	72.47476	72.424	-0.00070
$C_6H_6N_2O_2$	3-nitroaniline	72.47476	72.481	-0.00009
$C_6H_6N_2O_2$	4-nitroaniline	72.47476	72.476	-0.00002
$C_7H_7NO_2$	Aniline-2-carboxylic acid	80.90857	80.941	0.00041
$C_7H_7NO_2$	Aniline-3-carboxylic acid	80.90857	80.813	-0.00118
$C_7H_7NO_2$	Aniline-4-carboxylic acid	80.90857	80.949	0.00050
C_6H_6O	Phenol	61.75817	61.704	-0.00087
$C_6H_4N_2O_5$	2,4-dinitrophenol	77.61308	77.642	0.00037
C_6H_8O	Anisole	73.39006	73.355	-0.00047
$C_{10}H_{8}$	Naphthalene	90.74658	90.79143	0.00049
C_4H_5N	Pyrrole	44.81090	44.785	-0.00057
C_4H_4O	Furan	41.67782	41.692	0.00037
C_4H_4S	Thiophene	40.42501	40.430	0.00013
$C_3H_4N_2$	Imidazole	39.76343	39.74106	-0.00056
C5H5N	Pyridine	51.91802	51.87927	-0.00036
$C_4H_4N_2$	Pyrimidine	46.57597	46.51794	-0.00075
$C_4H_4N_2$	Pyrazine	46.57597	46.51380	0.00095
C_9H_7N	Quinoline	85.40453	85.48607	0.00093
C_9H_7N	Isoquinoline	85.40453	85.44358	0.00178
C_8H_7N	Indole	78.52215	78.514	-0.00010
$C_5H_5N_5$	Adenine	70.83735	70.79811	-0.00010

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Section V1

Software Program

The present invention relates to a system of computing and rendering the nature of at

least one specie selected from a group of diatomic molecules having at least one atom that is
other than hydrogen, polyatomic molecules, molecular ions, polyatomic molecular ions, or
molecular radicals, or any functional group therein, comprising physical, Maxwellian solutions
of charge, mass, and current density functions of said specie, said system comprising:
processing means for processing physical, Maxwellian equations representing charge, mass,
and current density functions of said specie; and an output device in communication with the
processing means for displaying said physical, Maxwellian solutions of charge, mass, and
current density functions of said specie.

In one embodiment, for example, the system comprises five components: (1) the graphical user interface (GUI); (2) the routine for parsing between an input chemical structure or name and taking the input and activating a routine to call up the parts of the molecule (functional groups), which are used for determining the energies and structure to be rendered; (3) the functional-group data base that has an organization of the theoretical solutions; (4) the rendering engine, which calculates and enables manipulations of the image, such as a three-dimensional model in response to commands, as well as responds to commands for data parameters corresponding to the image such as bond energies and charge distribution and geometrical parameters; and (5) data transfer system for inputting numerical data into or out of the computational components and storage components of the main system. The system further comprises spreadsheets with solutions of the bond parameters with output in any standard spreadsheet format. The system also comprises a data-handling program to transfer data from the spreadsheets into the main program.

The output may be, for example, at least one of graphical, simulation, text, and numerical data. The output may be the calculation of at least one of: (1) a bond distance between two atoms; (2) a bond angle between three of the atoms; (3) a bond energy between two atoms; (4) orbital intercept distances and angles; and (5) charge-density functions of atomic, hybridized, and molecular orbitals, wherein the bond distance, bond angle, and bond energy are calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration.

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In other embodiments, the charge, current, energy, and geometrical parameters are output to be inputs to other programs that may be used in further applications. For example, the data of heats of formation may be input to another program to be used to predict stability (existence of compounds) equilibrium constants and to predict synthetic pathways. That is, a 5 novel composition of matter may be discovered by calculating at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of 10 atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration. The charge and current density functions may be used to predict the electric and magnetic fields of the species to determine other properties due to the interaction of the fields between species. These fields and the predictions of field interactions may be computed using Maxwell's equations. In one 15 embodiment, finite-element analysis is used to predict or calculate the interaction and resulting properties, such as the freezing point, boiling point, density, viscosity, and refractive index. Furthermore, the output data can be used to give thermodynamic, spectroscopic, and other properties, aid in drug design and other applications with or without direct visualization. Furthermore, the data can be input into other programs of the system, which calculate 20 thermodynamic and other properties, or performs a simulation, such as a chemical reaction or molecular dynamics.

The output data may be used to predict a composition of matter comprising a plurality of atoms, the improvement comprising a novel property or use discovered by calculation of at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration. The novel property, for example, may be a new pharmaceutical use, or stability at room temperature of a novel arrangement of atoms or ions.

In one embodiment, the output device of the system is a display that displays at least one of visual or graphical media. The display may be at least one of static or dynamic. At least one of vibration, rotation, and translation may be displayed. The displayed information

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may be used for at least one of modeling reactivity, predicting physical properties, and aiding in drug and material design. The output device may be a monitor, video projector, printer, or one-, two- or three-dimensional rendering device. The displayed information may be used to model other molecules and provides utility to anticipate their reactivity and physical properties.

Additionally, data may be output and used in the same and additional applications as the rendered models and representations of the calculated physical solutions. The processing means of the system may be a general-purpose computer. The general-purpose computer may comprise a central processing unit (CPU), one or more specialized processors, system memory, a mass storage device such as a magnetic disk, an optical disk, or other storage device, an input

10 means. The input means may comprise a serial port, USB port, microphone input, camera input, keyboard or mouse. The processing means comprises a special purpose computer or other hardware system. The system may comprise computer program products such as computer readable medium having embodied therein program code means. The computer readable media may be any available media which can be accessed by a general purpose or

15 special purpose computer. The computer readable media may comprise, for example, at least one of RAM, ROM, EPROM, CD ROM, DVD or other optical disk storage, magnetic disk storage or other magnetic storage devices, or any other medium that can embody the desired program code means and which can be accessed by a general purpose or special purpose computer. The program code means may comprise executable instructions and data, which

20 cause a general purpose computer or special purpose computer to perform a certain function of a group of functions. Commercial examples of suitable program language includes, for example, C++, C, JAVA, FORTRAN, Python and Assembly Languages, programmed with an algorithm based on the physical solutions, and the computer may be a PC, mainframe, supercomputer, or cluster of computers. Commercial examples of suitable programs include,

25 for example, APIs like OpenGL, DirectX, FOX GUI toolkit, and Qt. This program may be developed to run on at least one of operating systems like Windows XP, Windows 2000, Windows Vista, MAC OS, MAC OS X, Linux, Unix, Irix and other Unix-type operating systems.

Millsian software is designed to render 3-D models of molecules, molecular ions,
30 molecular radicals, functional groups thereof, and related structure and property information
and produce useful data output and application of the parameters of these species, wherein the
nature of their bound electrons and chemical bonds are solved using Dr. Randell L. Mills'
Classical Quantum Mechanics theory described in the reference: R. L. Mills, "The Grand
Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional

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Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834; posted at

http://www.blacklightpower.com/bookdownload.shtml, which is incorporated by this reference in its entirety. Figure 76 provides a flow chart diagram, which is an example of a software

5 system that can be utilized for this purpose, which example is not intended to limit the scope of the disclosed inventions. The main parts of this exemplary software system illustrated in Figure 76 will now be further explained:

Start: A user can start the program by running an executable program file. That might be done, for example, by double clicking the program icon on a Windows-based operating system, or typing the name of the executable file on the command line and pressing the 'Enter' key on a Linux or Unix operating system. The program initially starts by reading data files located in specific directories. The names of those directories and locations are fixed according to the type and format of the data files.

Data files: There are two types of data files used in the software system: functional group data files and molecule data files. Functional group data files contain information about various functional groups. Functional groups are the basic bonding elements or units that each typically comprise an atom, or at least two atoms bound together as found within a molecule (e.g. -Cl, C=C, C=O, CH3). Functional groups typically dictate or define properties and structure of the molecule. Similar functional groups in different molecules typically react in similar ways when subjected to a particular set of reaction conditions. Molecule data files contain information about molecules, molecular ions, and molecular radicals. These data files are processed according to their file formats.

File formats: Millsian software employs two kinds of file formats for storing

25 information about the structure, energies and names of molecules and functional groups: rawdata format and hierarchical format. In a raw-data file, all information is stored as is, below
the header describing the type of information. As shown in the Table below, for example, the
names of the molecule or functional group are listed below the #NAMES header. The names
and positions of the atoms are listed below the #ATOMS header, and so on.

```
#NAMES
      CH3
      Alkane CH3
      #SMILES
 5
      C-
      #ATOMS
      1
             \mathbf{C}
                    0
                          0
                                 0
      2
             Η
                    1.9775 -0.698 0
      3
             H
                    -0.9888
                                 -0.698 1.712
      4
             Η
                    -0.9888
                                 -0.698 -1.712
10
      #AO
                    0.171 2
      1
             1 1s
      2
             1 2sp3 0.864 -1
      #BONDS
             12
                           1.649
      1
                    1
      2
             13
                    1
                           1.649
      3
                    1
15
             14
                           1.649
      #BONDAXES
                          90
             1
                    1
                                 0
                                        0
      #DATA
      RCH bond angle: 109.44°
      CH bond length: 2.097 a
20
      HFORM: 12.492
```

Most of the functional groups files and some simple molecule files are stored in raw data format. The other file format used with the Millsian software system, the hierarchical file format, represents the information in a graph style, in which nodes are connected to other nodes through links. This format is designed to construct molecules by attaching different functional groups in a desired manner. Using this file format, the user can construct complex molecules built from solved functional groups.

For example, as shown in the Table below, the pentane data file includes a #GROUPS header below which is list all of the functional groups that form a part of the pentane molecule.

30 Under the #GROUP_LINKS header is information about how these functional groups are connected to each other to construct pentane.

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				 	 	 _
#NAM						
#SMII						
#GRO 1 2 3 4 5	C- -C- -C- -C- -C-					
#GRO 1 2 3 4	OUP_LI 11 22 32 42	2 1	180 180 180 180			

5

10

Processing data files: As further shown in the flow diagram of Figure 76 for the exemplary Millsian software system, the program first processes the functional group data file and constructs the functional-group objects, which are complete 3-D representations of the functional groups and their related information supplied in the corresponding file. These objects are then ready to be visually displayed through use of a molecule viewer. Next, the program processes the molecule data file. If the molecule date file is in raw-data format, then the program makes a molecule object directly from it. If the file is in hierarchical format, then the program calculates geometric parameters from listed functional groups. The program stores all functional-group objects and molecule objects using internal data structures.

Visualization/ User Interactions: As shown in Figures 77 and 78, the molecule viewer displays the functional-group objects and molecule objects and provides basic interaction capabilities with the displayed objects, such as rotating, scaling, and moving the objects. The molecule viewer also provides other visualization options, such as viewing molecules in wire frame mode, viewing coordinate axes, and changing of the transparency and lighting. The user, for example, can also select parts of a molecule for visualization, like a nucleus, atomic orbital, molecular orbital, or bond axis. The viewer also includes a drop down information window, which provides, for example, related information about molecules, such as bond angles, component functional groups, and total heat of formation. In one embodiment, a user can create new molecules by joining functional groups. For this purpose, the user can select a

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first functional group. Next, the user can select an open bond from the functional group where the user desires to attach another group. Next, the user can select another or the same functional group, followed by selecting an open bond from the other group. The user can join the two selected functional groups at the selected open bonds by clicking on 'Join Groups'.

5 This method of joining functional groups at open bonds can be repeated to form the desired molecule.

SMILES input: The Simplified Molecular Input Line Entry Specification or SMILES is a specification for unambiguously describing the structure of chemical molecules using short ASCII strings. Through the user interface, a user can enter SMILES to construct molecules, provided the new molecule comprises functional groups that are in the database. Once a SMILES is entered, a parser reads in and breaks it down into component functional groups. The software system then attaches the component functional groups to create the new molecule object, which can then be viewed using the molecule viewer.

While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.

CONTINUOUS-CHAIN ALKANES ($C_n H_{2n+2}$, $n = 3, 4, 5...\infty$)

The continuous-chain alkanes, $C_n H_{2n+2}$, are the homologous series comprising terminal methyl groups at each end of the chain with n-2 methylene (CH_2) groups in between:

$$CH_3(CH_2)_{n-2}CH_3$$
 (15.109)

- 5 C_nH_{2n+2} can be solved using the same principles as those used to solve ethane and ethylene wherein the 2s and 2p shells of each C hybridize to form a single 2sp³ shell as an energy minimum, and the sharing of electrons between two C2sp³ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Three H AOs combine with three carbon 2sp³ HOs and two H AOs combine with two carbon 2sp³ HOs to form each methyl and methylene group, respectively, where each bond comprises a H₂-type MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. The CH₃ and CH₂ groups bond by forming H₂-type MOs between the remaining C2sp³ HOs on the carbons such that each carbon forms four bonds involving its four C2sp³ HOs. For the alkyl C-C group, E_T(atom-atom, msp³.AO) is -1.85836 eV where both energy contributions are given by Eq. (14.513). It is based on the energy match between the C2sp³ HOs of the chain comprising methylene groups and terminal methyl groups.
- The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of straight-chain alkanes are given in Tables 15.4, 20 15.5, and 15.6, respectively. The total energy of each straight-chain alkane given in Table 15.7 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.6 corresponding to functional-group composition of the molecule. The bond angle parameters of straight-chain alkanes determined using Eqs. (15.79-15.108) are given in Table 15.8. In this angle table and those given in subsequent sections when c_2' is given as the ratio of two values of

25 c_2 designated to Atom 1 and Atom 2 and corresponding to $E_{Coulombic}$ of Atom 1 and Atom 2,

respectively, then $c_2' = \frac{c_2(Atom\ 2)}{c_2(Atom\ 1)}$.

Table 15.4. The geometrical bond parameters of straight-chain alkanes and experimental values [1]. Parameter $C = C - H(CH_3)$ $C = H(CH_2)$ Group Group (C-H propane) (C-H propane)
1.177 (C-H butane) (C-H butane)
1.27295 (1.29569 1.67122 1.05553 1.11713 Group 1.64920 1.04856 1.10974 1,532 (propane) 1,531 (butane) 2.12499 1,45744 1.54280 1.54616 Exp. Bond Length (A) $c'(a_0)$ Bond Length 2c'(A) $a \begin{pmatrix} a_0 \end{pmatrix}$ h,c (a_0)

Table 15.5. The MO to HO intercept geometrical bond parameters of straigh	intercept ge	ometrical bond p	parameters of str	aight-chain alkar	ght-chain alkanes. E_r is $E_r(atom-atom,msp^3.AO)$	tom – atom, msp	$\sigma^3 AO$.								
Bond	Atom	E_{τ} (eV) Bond 1	E_T (eV) Bond 2	E_r (eV) Bond 3	E ₇ (eV) Bond 4	Final Total Energy C2sp³ (eV)	$r_{usind} = r_{usind} = r_0$	$\begin{pmatrix} r_{famt} \\ (a_0) \end{pmatrix}$	Erador (C2sp²) (eV) Final	$E(C2xp^3)$ (eV) Final	(o) (e)	(°)	(°)	d_i (a_c)	$\begin{pmatrix} d_2 \\ (a_0 \end{pmatrix}$
$C-H\left(CH_{3}\right)$	Ü	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\left(CH_{2}\right)$	Ü	-0.92918	-0.92918	0	0	-153,47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$H_1C_a - C_bH_2CH_2$	c"	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0,38106
$H_3C_n - C_3H_2CH_2$	ڻ	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Table 15.6. The energy parameters	(eV) of functional	groups of straight-c	hain alkanes.
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Parameters	C-C		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		Group	Group	Group
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$n_{\rm l}$	1	3	2
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	n_2	0	2	1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	n_3	0	0	0
$\begin{array}{c} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \\$	C_1	0.5	0.75	0.75
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C_2	1	1	11
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	c_1	1	1	1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	c_2	0.91771	0.91771	0.91771
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<i>c</i> ₃	0	0	1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<i>c</i> ₄	2	1	1
$\begin{array}{c} C_{1o} \\ C_{2a} \\ C_{2a} \\ C_{2a} \\ C_{2a} \\ C_{2b} \\ C_{2b$	<i>C</i> ₅	0	3	2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C ₁₀	0.5	0.75	0.75
$\begin{array}{c} V_{e} \ (eV) \\ V_{p} \ (eV) \\$		1	1	. 1
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$V_{e}(eV)$	-28.79214	-107.32728	-70.41425
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		9.33352	38.92728	25.78002
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	T(eV)	6.77464	32.53914	21.06675
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$V_m(eV)$	-3.38732	-16.26957	-10.53337
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	E(AOIHO) (eV)	-15.56407	-15.56407	-15.56407
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Delta E_{H_2MO}(AO/HO)$ (eV)	0	0	0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$E_{T}(AOIHO)$ (eV)	-15.56407	-15.56407	-15.56407
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$E_T(H_2MO)$ (eV)	-31.63537	-67.69451	-49.66493
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-1.85836	0	0
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		-33.49373	-67.69450	-49.66493
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		9.43699	24.9286	24.2751
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		6.21159	16.40846	15.97831
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		-0.16515	-0.25352	-0.25017
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.12312 [2]		0.35532 (Eq. (13.458))
$\begin{array}{c ccccc} E_{mag} & (eV) & 0.14803 & 0.14803 & 0.14803 \\ E_{T} & (\textit{Group}) & (eV) & -33.59732 & -67.92207 & -49.80996 \\ E_{\textit{Initial}} & (c_{4} & \textit{AOI HO}) & (eV) & -14.63489 & -14.63489 \\ E_{\textit{mitial}} & (c_{5} & \textit{AOI HO}) & (eV) & 0 & -13.59844 & -13.59844 \end{array}$	\overline{E}_{osc} (eV)	-0.10359	-0.22757	-0.14502
E_T (Group) (eV) -33.59732 -67.92207 -49.80996 $E_{initial}$ (c_4 AO/HO) (eV) -14.63489 -14.63489 -14.63489 $E_{initial}$ (c_5 AO/HO) (eV) 0 -13.59844 -13.59844		0.14803	0.14803	0.14803
$E_{milial}(c_{4} \text{ AO/HO}) (eV)$ -14.63489 -14.63489 -14.63489 $E_{milial}(c_{5} \text{ AO/HO}) (eV)$ 0 -13.59844 -13.59844		-33.59732	-67.92207	-49.80996
$E_{milial}(c_{s} AO/HO) (eV)$ 0 -13.59844 -13.59844		-14.63489	-14.63489	-14.63489
		0	-13.59844	-13.59844
	$E_{D}(Group)$ (eV)	4.32754	12.49186	7.83016

Table 15.7. The total bond energies of n-alkanes calculated using the functional group composition and the energies of Table 15.6 compared to the experimental values [3].

Relative	Епог		-0.00085	-0,00036	-0.00017	-0.00019	-0.00013	-0.0000	-0.00012	-0.00003	0.00004	-0.00008	0.00008
Experimental	Total Bond	Energy (eV)	41.434	53.61	65.77	77.93	60.06	102.25	114.40	126.57	138.736	150.88	223.85
Calculated	Total Bond Energy	(eV)	41.46896	53.62666	65.78436	77.94206	90.09976	102.25746	114.41516	126.57286	138.73056	150.88826	223 83446
Ŧ	;°		_	7	'n	4	'n	9	7	00	6	9	91
E	<u>.</u>		2	7	2	2	7	7	7	2	7	7	,
ن-ر ن-ر)		2	m	4	ı,c	9	7	00	6	. 2	=	18
Name			Propane	Butane	Pentane	Hexane	Heptane	Octane	Nonane	Decane	Undecane	Dodecane	Octoberane
Formula			350	i i	ČE,	CH.C	1. T.	H.C	H L L L L L L L L L L L L L L L L L L L	CoHi	C.F.	ChH ₂	1 T

Table 15.8. The bond angle parameters of straight-chain alkanes and experimental values [1]. In the calculation of $\theta_{\rm e}$, the parameters from the preceding angle were used. $E_{\rm r}$ is $E_{\rm r}(atom-atom,msp^3.AO)$.

\ -\ ;	Exp. θ	107 (propane)	112 (propane) 113.8 (butane)	111.0 (butane)			
Г	(3) 0	108.44	110.49	110.49	109,50	109.44	109.44
	θ ₂	i					
-[θ ¹ (ο)						
-[θ (ο)		15.69	69.51		70.56	70.56
. 1	$E_{ au}$ (eV)	0			0		:
	`v'	1.15796			1.15796		
	ប	0.75	. 18		0.75		
	ΰ	-			-		
.,	ບັ ່	-			1		
	C ₂ Atom 2.	-			· •		
יו נווס סמוס וו	C ₂	0.86359			0.86359		
Table 15.8. The boild digit parameters of straight-drain areness and experimental values [1]. In the deadless of the	Atom 2 Hybridization Designation (Table 15.3.A)	н			Ξ		
ייייישלים ה	Eraulombid Atom 2	Ħ			н		
ש כשומשווים מושווים	Atom 1 Hybridization Designation	7			7		
יייקומוופ וט	E Contombic Atom 8	15.75493 C_			15.75493 C_		
מווובובוא	2c¹ Teminal Atoms (a₀)	3,4252			3.4252		
merc ba	2c' 2c' Bond 2 Terminal (a ₀) Atoms	2.1110			2.0971		
nue pond	2c' Bond ((a ₀)	2.11106 2.1110 3.4252			2.09711		
1 able 15.8.	Atoms of Angle	Methylene ZHC "H	2,50,07	H"D"D7	Mediy.1 2.09711 2.0971 3.4252 13.75493 C.,	20 07	

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BRANCHED ALKANES ($C_n H_{2n+2}$, $n = 3, 4, 5...\infty$)

The branched-chain alkanes, C_nH_{2n+2} , comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene 5 functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl ($(CH_3)_2 CH$) and t-butyl ($(CH_3)_3 C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-alkane groups are solved using the same principles as those 10 used to solve the methyl and methylene functional groups wherein the 2s and 2p AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two C2sp3 HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. $E_T(atom-atom, msp^3.AO)$ of each C-C-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is $-1.85836 \, eV$ or $-1.44915 \, eV$ based on 15 the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, -0.92918 eV (Eq. (14.513), or methyl, -0.72457 eV (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of branched-chain alkanes are given in Table 15.9. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. 20 (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkanes are given in Tables 15.10, 15.11, and 15.12, respectively. The total energy of each branched-chain alkane given in Table 15.13 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.12 corresponding to functional-group composition of the molecule. The bond angle parameters of branched-chain alkanes determined using Eqs. (15.79-15.108) are given in Table 15.14.

Table 15.9. The symbols of functional groups of branched alkanes.

Functional Group	Group Symbol .
CH₃ group	$C-H$ (CH_3)
CH ₂ group	$C-H$ $\left(CH_{2}\right)$
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

0,45117

1.83879

1.97162

0.50570 0.51388

1.95734

21.74

0.18708 0.37326

1.23564 1.35486 1.42988

41.48 35.84 31,37 30.08 26,06 21.90

 $\begin{pmatrix} a_1 \\ a_0 \end{pmatrix}$

(a) 1, a

ر. (ق. م

0,49298

1.94462

22.66

0.49298 0.47279

22.66

1,97162 1,94462

21.90

C-C (f) Group	2.10725	.45164	1.53635	532	(propane)	butane)	.52750	0.68888
							_	_
C-C (e)	2.10725	1,45164	1.53635	1.532	(propane) 1.531	(butane)	1,52750	0.68888
C-C (d) Group	2.12499	1.45744	1.54280	1.532	(propane) 1.531	(butane)	1.54616	0.68600
C-C (c) Group	2.10725	1.45164	1.53635	1.532 .	(propane) 1.531	(butane)	1.52750	0 68888
C' - C' (b) Group	2.12499	1.45744	1.54280	1.532	(propane) 1.531	(butane)	1.54616	0 68600
Parameter $C = H(CH_3)$ $C = H(CH_2)$ $C = H$ $C = C(a)$ Group Group	2.12499	1.45744	1.54280	1.532	(propane)	(butane)	1.54616	0 68600
C - H Group	1.67465	1.05661	1.11827		1.122 (isohutane)	(2)	1,29924	20053.0
$('-H)$ (CH_1) Group	1.67122	1.05553	1.11713	1 107	7-2)	(C - H butane)	1.29569	02150
$C - H\left(CH_3\right)$ Group	1.64920	1,04856	1,10974	1 107	(C - H propane)	(C-H butane)	1.27295	002070
Parameter	$a\left(a_{\scriptscriptstyle 0}\right)$	c' (a _a)	Bond Length 2c' (A)	L	Exp. Bond Length	(F)	h,c (a,)	

15.11. The MO to HO intercept	incal bond	parameters of o	alleneu-chaill al	geometrical bonu parameters of pranticular channels. Askir, and the change groups. Askir, and the change of the ch	are to a mind	Final Total	14.	, -	F (C2m)	(6,000)	,θ	θ	- 1
Bond	Atom	E _T (eV) Bond 1	(eV) Bond 2	ε _τ (eV) Bond 3	(eV) Bond 4	Energy ('2xp'	$\begin{pmatrix} a_0 \end{pmatrix}$	(a _a)	(eV) Final	(eV) Final	. ©		
('-H (CH.)	į	-0.92918	0	0	0	-152,54487	0.91771	0.86359	-15.75493	-15,56407	77.49	102.51	
C-H (CH,)	ن	41 92918	-0.92918	0	С	-153.47406	0.91771	0.81549	-16.68412	-16,49325	68.47	111.53	
('-H (CH)	Ü	-0.92918	-0.92918	-0.92918	a	-154,40324	17716.0	0.77247	-17.61330	-17.42244	61.10	118.90	1
$H_1^{\zeta}C_{\mu}^{\zeta}C_{\mu}^{\zeta}H_1^{\zeta}H_1^{\zeta}$	")	-0,92918	c	C	0	-152 54487	17716.0	0.86359	-15.75493	-15.56407	63.82	116,18	
$H_1^{C}C_1^{C}H_2^{C}H_2$ – $CC_1^{C}C_1^{C}H_2^{C}$	(,	-4:9291R	-0.92918	0	O	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	
$R = H_2C_aC_b(H_2C_c - R)HCH_2 - CC_aC_b(H_2C_c - R)$	ر.*	-0.92918	-0.92918	-0.92918	D	-154.40324	17710.0	0.77247	-[7.61330	-17.42244	48,30	131.70	- 1
$R - H_2C_a(R^- + H_2C_a)C_b(R^n - H_2C_c)CH_2 - CC_2C_2(R^0)$	۲,	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	17716.0	0.75889	-17.92866	97757.71-	48.21	131.79	- 1
$isoC_{i}C_{i}(H_{2}C_{i}-R^{i})HCH_{2}-$	ئ	-0.92918	-0.92918	-0.92918	9	-154.40324	17716.0	0.77247	-17.61330	-17.42244	48.30	131.70	
$Ier(C_a(R^- H_1C_a)C_b(R^- H_1C_c)CH_1 - C_c)$	ڻ	-0.72457	-11.72457	-0.72457	-41.72457	-154.51399	17716.0	0.76765	-17.92866	-17.73779	50.04	129.96	
(C-C, C) (C-C, C)	ڻ	-0.72457	-0.92918	-0.92918	ç	-154,19863	177160	0.78155	-17.40869	-17,21783	52.78	127.22	- 1
(C - C)	ئ.	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	0.91771	0.76765	-17.92866	-17.73779	50,04	129.96	

Parameters CH_1 CH_2 $C-H$ Group	CH ₃ Group	CH ₂ Group	Group	C ~ C (a) Group	C – C (b) Group	C - C (c) Group	C-C (d) Group	C C (e) Group	C – C (f) Group
$n_{\rm f}$	3	2	1	1	1	П	,		1
n_z	2	1	0	0	0	0	0	0	0
n,	0	0	0	0	0	0	0	0	0
c_1	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ζ,		1	1	1					1
<i>c</i> ₁	1	. 1	1	1	,	1	1		
c_2	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
້ຽ	0	_	-	0	0	0	1	-	0
ั้ง	-		1	2	2	2	2	2	2
ς.	3	2	1	0	0	0	0	0	0
C _I ,	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C _{2,} ,	-	-	1	1	1	-	1	I	1
V, (eV)	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T(eV)	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{m} (eV)	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(-normo) (eV)	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
ΔE_{H_2MO} (normo) (eV)	0	0	0	0	0	0	0	0	0
$E_{r}(\omega \omega)$ (eV)	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(u_2 s m)$ (eV)	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(alom - alom, msp^3.AO)$ (eV)	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{T}(\omega)$ (eV)	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega \left(10^{15} rad / s\right)$	24.9286	24.2751	24.1759	9.43699	9,43699	15.4846	9.43699	9.55643	9.55643
E_{κ} (eV)	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
\overline{E}_{n} (eV)	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{ ext{Kub}}\left(eV ight)$	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312	0.17978	0.09944	0.12312 [2]	0.12312	0.12312
$\overline{\vec{E}}_{ m ac}$ (eV)	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{ m neg}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{T}(ext{tiranp})$ (eV)	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Equital (c. 101110) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489
Emitted (c. 101110) (eV)	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(\omega_{mp})$ (eV)	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.13. The total bond energies of branched alkanes calculated using the functional

14016 13.1	Table 15.15. The total bond energies of branched alkanes calculated	nched alkanes	calculated usin	g the functiona	using the functional group composition and the energies of Table 15.12 compared to the experimental values [3]	thon and the ent	rgies of Table	15.12 compare	d to the experir	nental values [3].		
rormula	Name	CH_{s}	CH_{2}	CH	C - C (a)	C-C (b)	C-C (6)	C-C (q)	C-C (e)	C-C(t)		Experimental	Relative Error
											Total Bond	Total Bond	
C,H _{III}	Isobutane	3	0	_	0		c	0		0	בייניונים (בא)	Lucigy (ev)	
C ₅ H ₁₂	Isopentane		-	_		1 417			• •	,	77660.66	25.093	-0.0000
CsH ₁₂	Neopentane	4	С	0	-	_	-		,	> <	2000000	02.043	-0.00021
CaHla	2-Methylpentane	· erq	, 7	. –	, ,	> "	+ <	> <	> 0	-	65.86556	65.992	0.00195
CH	3-Methylnentane	۰ ۳	٦,	•	4 (. .	> <	- 0	. '	0 '	78.01462	78.007	-0.00010
t HO	2 2-Dimethylbutane	٦ ج	4	٠.	7 -	n (۰ د	- -	0	0	78.01462	616.11	-0.00046
CH.	2 3-Directhylbutana	r =	- c	> c	c	-	4 (0	0	0	78.02106	78.124	0.00132
7 17	2,2-Dinchlyloudie	† c	> (7 •	⊋ •	4	0	-	0	0	77.99581	78.043	0,00061
2118	2 Methylnexane	n (m (.	ימי	m	0	0	0	0	90.17232	90.160	-0.00014
בי בי	5-Methylhexane	~ 1) (m i	_	en ·	m	0	0	0	0	90.17232	90.127	-0.00051
ر ا ا	5-Ethytpentane	γ,	m		3	m	0	- 0	0	0	90.17232	801.08	-0 00072
C'H's	2,2-Dimethylpentane	4 .	7	0	7	0	4	, O	0	0	90,17876	90.276	0.00107
בי בי	2,2,3-1 rimethylbutane	'n.	0		0	7	n	0	0		90.22301	90.262	0.00044
5,4 k	Z,4-Dimethylpentane	4	_	2	0	9	0	0	0	0	90.24488	90,233	-0.00013
25 E	5,5-Unnethylpentane	4 (. 2	0	2	0	4	0	0	0	90.17876	90.227	0.00054
281 ₁₈	2-Metnyiheptane	· 1	4	_	4	m	0	0	0	0	102,33002	102.322	-0.00008
E. E. C.	3-Methylheptane	M I	4		4	m	0	0	0	0	102.33002	102.293	-0.00036
2 I I	4-Methylheptane	.u i	4		4	6	0	0	0	0	102,33002	102.286	-0.00043
× :	3-Ethylhexane	m ·	4	_	n	4	0	0	0	0	102,30169	102.274	-0.00027
۳. ت:	2,2-Dimethylhexane	4		0	m	0	4	0	0	0	102.33646	102.417	0.00079
. T	2,3-Dimethylhexane	4	2	2	2	4	0	-	0	0	102,31121	102.306	-0.00005
	2,4-Dimethylhexane	4.	7	7	_	9	0	0	0	0	102,40258	102,362	-0.00040
* !	2,5-Dimethylhexane	4	2 5	7	_	9	0	0	0	0	102.40258	102.396	-0,0006
81 I	2.4 Dimetrymexane	4 4	m d	0 (m	0	4	0	0	0	102.33646	102,369	0.00032
# T T	2 Colon 2 model	4 •	7 (7 (2	4	0	-	0	0	102,31121	102.296	-0.00015
* I	2 Educi 2	d 4	7 (7	7	4	0	-	0	0	102,31121	102.277	-0.00033
	2.7.3 Trimemyipentane	4 u	· .	٥.	in) ·	0	4	0	0	Q	102.33646	102,317	-0.00019
ž II	2,2,2-1 innemy penale	n •				7	m ·	0	0	-	102.38071	102,370	-0.00010
# H.	2 3 2 Trimethylpontale	n 4		- -	۰ د	n (4	0	0	0	102,40902	102.412	0.00003
	2,2,2-1 innemy penale	- v	- <		- ‹	7	m (0	0		102.38071	102.332	-0.00048
# H	2.2.3.7 - minetify politaire	· ·	> <	2	o •	Λ (٠ c	7	0	0	102,29240	102.342	0.00049
# H	2.2.5.7.7-1 ettametingjourane	. .	.	> (o (0 1	9	0	-	0	102,41632	102.433	0.00016
1 T	2,3,2 Tintellyllexalle	n •	•	~ ·	٥.	7	0	_	0	0	114.54147	114,551	0.00008
8 3	2,2-Distributionians	,	4 -	> (4	0	4	0	0 .	0	114.49416	114.455	-0.00034
2013	2.2.5.3-1 etrainemypeniane	٥,	– 6	o (- ·	Φ,	9	0		0	114.57402	114,494	-0.00070
2 T T T	2, 2, 3, 4-1 citainen yipentane	٥ ٧	5 -	7 (٥ (m (m	-	0		114.51960	114.492	-0.00024
6 H	2,2,4,4-1 citalifediyipellidire 2,3,3,4-7 citalifediyipellidire	o v	«	0 (.	o ·	× •	0	0	0	114.57316	114.541	-0.00028
200	2,2,2,4-1 en annemythemane	5 6	> `	~1 ·	o '	4	7	0	0	7	114.58266	114,484	-0.00086
	z-ivielitymonane	n 1	٠ و		9	m	0	0	0	0	126.64542	126.680	0.00027
C10122	3-ivietnyinonane	3	9	_	૭	r	0	0	0	c	126 64542	176 663	0 00014

107 (propane) 112 (propane) 113.8 (butane) 110.8 (isobutane) 111.0 (butane) 111.1 (isobutane) 110.8 (isobutane) 111.4 (isobutane) 111.4 (isobutane) $\mathop{\mathrm{Exp.}}_{(\circ)}\theta$ 109.50 109.44 111.27 107.50 110.67 111.27 © @ [5] Table 15.14. The bond angle parameters of branched-chain alkanes and experimental values [1]. In the calculation of θ_{ρ} , the parameters from the preceding angle were used. E_{T} is E_{T} (atom – atom, msp³.AO) θ₂ (0) θ₁ 72.50 70.56 69.51 69.51 و^{*} (ق -1.85836 -1.85836 E_T (eV) 0 0 0 0 0.81549 1,04887 1.15796 1.15796 1.04887 1.04887 ۍ, 0.75 0.75 0.75 0.75 0.75 \mathcal{C} 0.75 0.75 0.75 <u>ن</u> ---0.81549 0.91771 0.91771 c_2^{\prime} Atom 2 0.81549 0.87495 0.87495 0.86359 $c_{
m 2}$ Atom I Atom 2 Hybridization Designation (Table 15.3.A) 25 I -16.68412 - C_e -14.82575 -14.82575 C_c -14.82575 C_a Erantombic Atom 2 ů I I (Table 15.3.A) 25 1 'n Ś 9 -16.68412 C -15.55033 C_" -15.55033 C, Erantombie Atom l -15.75493 -15.55033 C_b -15.75493 2c'Terminal
Atoms (a_0) 3.4252 3.4252 4.1633 4.7958 4.7958 2.09711 2.91547 2.11323 2.09711 2,90327 2.11106 $\frac{2c^{1}}{\text{Bond 2}}$ 2.09711 2.91547 2.91547 2.91547 2,11106 2.90327 2c' Bond 1 (a,) $\begin{array}{c} ZC_{\mu}C_{\mu}H \\ ZC_{\mu}C_{\mu}C_{\mu} \\ \text{iso } C_{\mu} \\ ZC_{\mu}C_{\mu}H \\ \text{iso } C_{\mu} \\ \text{iso } C_{\mu} \end{array}$ רמ"כ"כ" מינו כ" Methyl ZHC_aH כ"כ"כ $ZC_{\mu}C_{\mu}H$ ZC"C"C ZC,C,H "C"C"C" Methy tene ZHC H Siso O

ALKENES
$$(C_n H_{2n}, n = 3, 4, 5...\infty)$$

The straight and branched-chain alkenes, C_nH_{2n} , comprise at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that 5 substitute for the hydrogen atoms of ethylene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, three distinct functional groups can be identified: C vinyl single bond to -C(C) = C, C vinyl single bond to -C(H) = C, and C vinyl single bond to $-C(C) = CH_2$. In addition, CH_2 of the $-C = CH_2$ moiety is an alkene functional group.

The alkyl portion of the alkene may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH₂), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds 15 can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkenes are equivalent to those in branched-chain alkanes. The solution of the functional groups comprises the hybridization of 20 the 2s and 2p AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two C2sp3 HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. $E_T(atom-atom, msp^3.AO)$ of the C=Cbond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene, $-2.26759 \, eV$, given by Eq. (14.247). $E_T \left(atom-atom, msp^3.AO\right)$ of each 25 C-C-bond MO in Eq. (15.52) is $-1.85836 \, eV$ or $-1.44915 \, eV$ based on the energy match between the C2sp3 HOs corresponding to the energy contributions equivalent to those of methylene, $-0.92918 \, eV$ (Eq. (14.513), or methyl, $-0.72457 \, eV$ (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of alkenes are given in Table 15.15. The 30 geometrical (Eqs. (15.1-15.5) and (15.41)), intercept (Eqs. (15.71-15.78)), and energy (Eqs.

(15.6-15.11) and (15.17-15.56)) parameters of alkenes are given in Tables 15.16, 15.17, and 15.18, respectively. The total energy of each alkene given in Table 15.19 was calculated as the sum over the integer multiple of each $E_D(G_{roup})$ of Table 15.18 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage 5, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(G_{roup})$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkenes determined using Eqs. (15.79-15.108) are given in Table 15.20.

.1	Group Symbol	2"2	(i)	(E) 7-1	(C+C: (III)	$C-H\left(CH_{2}\right) \left(t\right)$	$(-H \{CH_i\})$		$C-H\left(CH_{1}\right)$ (II)	H)	(;) (; (a)	(a) (b) (c)	(a) (c) (c)	(a) 3 - 3	(a)) · · ·	(1)
Table 15,15. The symbols of functional groups of alkenes	Functional Group	CC double bond	C vinyl single bond to -C(C)=C	C vinyl single bond to -C(H)=C	C vinyl single bond to -C(C))=CH2	CH, alkenyl group		CH; group	CH ₂ alkyl group	HO	CC bond (n-C)	CC bond (iso-C)	CC bond (tert-C)	CC (iso to iso-C)	CC (t to t-C)	CC (t to iso-C)

Group	2.10725		1.45164		1.53635		1 537	(propane)	(butane)		1.52750	00007 0	0.00000	
Group	2.10725		1,45164		1.53635		1 537	(propane)	(butane)		1.52750	00000	0.08888	
Group	7 17499	Z.121/	1.45744		1.54280			(propane)	1,531 (futtane)		1.54616		0.68600	
Group	20705 5	2.101.2	1.45164		1.53635		1	[.532 (propane)	1.531 (hutane)	(camma)	1 52750		0.68888	
Group Group	0.18100	2.12499	1 45744		1 54280			1.532 (propane)	1,531	(ontaine)	1 54616	010+01	0.68600	
Group		2.12499	1 45744	1,43744	1 64790	1,14240		1.532	1.531	(butane)	7,070	1,34010	0.68600	
Group		1.67465		1.05661		1.11827		1.133	(isobutane)			1.29924	2005	COCOTO
$C-H\left(CH_{2}\right)$ (ii)	Group	1 67122		1.05553		[11713	1 107	(C-H	propane)	(C-H	butane)	1.29569	031070	0.03139
$\begin{array}{c c} C-H\left(CH_3\right) & C- \\ Group & \end{array}$,	1 64930	07/10.1	1.04856		1.10974	1 107	(C-H)	propane)	H-))	butane)	1 27795	207171	0.63580
$C-H\left(CH_{2}\right)$	(1) (1) Group			1.04566		1,10668		1.10	(2-methy/propene)	(1.3-butadiene)		1 26364	1.20.34	0.63756
C-('(ii)		9,5,5	+		1.43087		1,508 (2-methylpropene)			00171	1,46439	0.69887		
('-(' (ii) Group			2.04740	1 43087	200	1.51437	1.508 (3-busine)		(2-Dulene)			1.46439	0.69887	
C:-('(i) Group			2.04740	1 42007	1.42007	1 51417							1.46439	0 40887
Table 15.16. The geometrical bond parameters of alternes are experience. Circl (1) $C' - C'$ $C' - C'$ Parameter $C = C - C' - C'$ Group $C = C'$; ;		1.47228	. 27,76	1,2002,1	1 34053	2504C.1	1.342	1.346	(2-butene)	1.349		0.75055	0.000
Table 15.16. The Parameter			a (a,)		c. (aº)	Bond Length	2c' (A)	i	9	(F)			60(0)	(8)

532

Bond	Atom	E	Ŀ	L	Į.	Final Total			(m)	1 2	10	0		,	-
,		(eV) Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C2sp³ (eV)	(a_a)	(a_a)	(eV) Final	e(c.sp) (eV) Final		s ⁻ €	ζ _ο (.)	$\begin{pmatrix} a_{i} \\ (a_{b}) \end{pmatrix}$	$\begin{pmatrix} a_2 \\ a_0 \end{pmatrix}$
$C_c(H)C_a = C_a(H)C_a$	<i>"</i>	-1.13380	-0.92918	٥	Û	-153.67867	17710.0	0,80561	-16.88873	-16.69786	127.61	52.39	58.24	0.77492	0.49168
$C_{\varepsilon}(H)C_{\omega} = C_{s}H_{z}$	ر ,	-1.13380	0	0	0	-152,74949	17716.0	0.85252	-15,95955	-15.76868	129.84	50.16	60.70	0,72040	0.54620
$C_{\epsilon}(C_{a})C_{s} = C_{b}H,C_{\epsilon}$	".)	-1,13380	-0.72457	-0.72457	0	-154,19863	17716.0	0.78155	-17.40869	-17,21783	126.39	53.61	56.95	0.80289	0.46371
$R_{\{C,h,H_1-C,J\}}(C) = C$ $(C-C,\{i\})$	ن.	-1.13380	-0.72457	-0.72457	0	-154,19863	17716.0	0.78155	-17.40869	-17.21783	60.88	119.12	67.72	1.81127	0.38039
$R_{C_a}H_1 - C_a(C) = C$ $(C - C \ (1))$ $R_{C_a}H_1 - C_a(C) = CH_1$ $(C - C \ (iii))$	ر.	-11,72457	816Z6;n-	. 6	G	-153.26945	17716.0	0.82562	-16.47951	-16.28864	0+79	112.60	31.36	1.74821	0.31734
$R_{i}C_{i}H_{j} - C_{i}(H) = C$ $(C - C_{i}(i))$	ر"	-1,13380	-0.92918	o	O	-153.67866	177160	0,80561	-16.88873	-16.69786	64.57	115.43	29.79	1.77684	0.34596
$R_{i}^{C}{}_{\mu}H_{2} - C_{\mu}(H) = C$ $(C - C_{i}(1))$	C,	-0.92918	-0.92918	0	0	-153.47405	17716.0	0.81549	-16.68411	-16.49325	65.99	114,01	30.58	1.76270	0.33183
$C-H\left(CH_{1}\right)$ (i)	i,	-1.13380	0	0	0	-152.74949	17716.0	0.85252	-15,95955	-15.76868	77.15	102.85	41.13	1.23531	0.18965
$C-H$ (CH_3)	Ü	-0,92918	. 0	D	0	-152.54487	17716.0	0.86359	-15,75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C - H\left(CH_2\right)$ (ii)	ن	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16,68412	-16,49325	68.47	111.53	35.84	1.35486	0.29933
C-H (CH)	i.	-0.92918	-0.92918	-0.92918	0	-154 40324	17716.0	0.77247	-17.61330	-17,42244	61.10	118.90	31.37	1.42988	0.37326
H_1C,C,H_2CH_2- (C-C,C,a)	نُّ	-0.92918	c	. 8	0	-152.54487	17716.0	0,86359	-15.75493	-15,56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C,C_3H_2CH_2 - (C-C,C_3H)$	C,	-0.92918	-0 92918	c	c	-153,47406	177160	0.81549	-16.68412	-16.49325	\$6.41	123.59	26.06	068067	0,45117
$R - H_2C_n'C_b(H_2C_s - R')HCH_2 - (C - C'(b))$	نٔ	-0.92918	0.92918	-0.92918	Ü	-154,40324	0.91771	0.77247	-17,61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2 C_n (R^n - H_2 C_d) C_n (R^n - H_2 C_c) C H_2 - (C - C_1 C_0)$	C,	-0,92918	-0.72457	-0.72457	-0.72457	-154.71860	17716.0	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_{\mu}C_{\mu}(H_{2}C_{\mu}-R^{2})HCH_{2}-(C-C_{\mu}-C_{\mu})$	C,	-0.92918	-0.92918	-0.92918	В	-154,40324	17716.0	0.77247	-17,61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tenC_{u}(R'-H_{2}C_{u})C_{b}(R''-H_{2}C_{c})CH_{2}-(C-C_{c}(e))$	نْ	-0.72457	-0 72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$ter(C,C,\{H_1C_c-R'\}HCH_2-(C-C,\{f\})\}$	ن '	-0.72457	-0.92918	-0.92918	-0	-154,19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$i_{KH}C_{\mu}(R-H_1C_{\mu})C_{\mu}(R^{\mu}-H_2C_{\nu})CH_1 - (C-C^{\mu}(f))$	ڻ	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1,94462	0.49298

Table 15.17. The MO to HO intercept geometrical bond parameters of alkenes. R_i is an alkyl group and $R_iR_i^*R^*$ are H or alkyl groups. E_t is $E_t\left(atom-atom,msp^3.AO\right)$.

Table 15.18. The energy parameters (eV) of functional groups of alkenes.	s (eV) of func	ctional groups	of alkenes.											9,0
Parameters	C = C Group	C-C (i) Group	C-C (ii)	C-C (iii)	CH ₂ (i)	CH, Group	CH ₂ (ii)	C – H Group	C-C(a) Group	(b) Group	Group	Group	Group	Group
n,	2	-		-	2	3	2	-	-	1	1	1	1	1
n,	0	0	0	0	-	2	_	0	0	0	0	0	0	0
n,	0	0	0	0	0	0	0	0	0	0	0	0	0	0
, C	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0,5	0.5	0.5	0.5	0.5	0.5
3	17716.0		-		-		1	1	1	1	1	1	-	
נ'	-	-	-	_	1	-	-	-		1	1	1	-	-
3	0.91771	17716.0	0.91771	0.91771	0.91771	- 0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
	0	-	0	_		0	-	1	0	0	0			0
, c,	4	2	2	2	-		1	-	2	2	2	2	2	2
	0	0	0	0	2	3.	2	-	0	0	0	0	0	0
, 5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	5.0	0.5	0.5	0.5	0.5	0.5
	17710	-	_		-		_		1	1	1	-	1	-
V, (eV)	-102,08992	-30.19634	-30.19634	-30.19634	-72.03287	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	21.48386	9.50874	9.50874	9.50874	26.02344	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	34.67062	7.37432	7.37432	7.37432	21.95990	32.53914	21.06675	10.48582	.6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_ (eV)	-17.33531	-3.68716	-3.68716	-3.68716	-10.97995	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3,38732	-3.45250	-3.45250
E(somo) (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
ΔΕ _{Π,MO} (JOIND) (eV)	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$E_{\tau}(\text{JOINO})$ (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15,56407	-15.35946	-15.35946
$E_{\tau}(\mu_{z}\omega)$ (eV)	-63.27075	-31.63534	-31.63534	-31.63534	-49.66437	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31,63537	-31.63535	-31.63535
$E_r(atom - atom, msp^3. AO)$ (eV)	-2.26759	-1.44915	-1.85836	-1.44915	0	0	0	0	-1.85836	-1.85836	-1,44915	-1.85836	-1.44915	-1.44915
$E_T(1,m)$ (eV)	-65.53833	-33.08452	-33.49373	-33.08452	-49.66493	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (10 ¹⁵ rad/s)	43.0680	9.97851	16.4962	15876.6	25.2077	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_{κ} (eV)	28.34813	6.56803	10.85807	6.56803	16.59214	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{\mathcal{E}}_{D}$ (eV)	-0.34517	-0.16774	-0.21834	-0.16774	-0.25493	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{K^{\prime\prime}b}$ (eV)	0.17897	0.15895	0.09931	0.09931	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312	0.12312 [2]	0.12312 [2]
E. (eV)	-0.25568	-0.08827	-0.16869	-0.11809	-0.07727	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{\rm ling}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E_{τ} (inup) (eV)	-66.04969	-33.17279	-33.66242	-33.20260	-49.81948	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Emilia (c. MIIIO) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Eminal (c101110) (eV)	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
E_{D} (simp) (eV)	7.51014	3.75498	4,39264	3.78480	7.83968	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

composition and the energies of Table 15.18 compared to the experimental values [2]. The magnetic energy $E_{\rm acc}$ that is subtracted from the weighted sum of the $E_{\rm b}(c_{\rm acc})$ (eV)

C.3.H. Propene C.3.H. 1-Butene C.3.H. trans-2-Butene	2			.)-)	ر <u>-</u> ر	CH, (i)	ĊĦĊ	CH, (i)	H.	010	ပ ပ	ن در:	ပ ပ	ن ا د	(I)	201	Tett Deed	Tatal Bond	Linn
			Θ	E	(•		(g)	(<u>a</u>)	(0)	(q)	(e)			Energy (eV)	Energy (eV)	7
		c	c	-	0		-	0	 -	0	0	0	0	0	0	0	35,56033	35.63207	0.00201
	<u> </u>	-	s c	٠.						-	0	0	0	0	0	0	47.71803	47.78477	0.00140
	alic D.:tests		0 0	, ,		. c	. 6	0	7	0	0	0	0	0	0	0	47.93116	47,90395	-0.00057
	-Du(cile		•	۱ د	, ,		, ,	c	¢	c	0	0	0	0	0	0	47.90314	47.96096	0.00121
	ene	 .	-	> -	۷ د		4	۰ ر	· -	· –			0	0	0	0	59.87573	59.95094	0.00125
	ene	_	0	-	۰ د	(¢	7 -	- (- -	ء د		· -			· c	60 08886	60.06287	-0.00043
	irans-2-Pentene	_	0	7	0 (۰ د	~1 6	 .	٧ (> <	> <	> <	۰ د	· c	• =	60 06084	60.09707	0.00060
	2-Methyl-1-butene	_	0	0	7	-	7		۰ د	- •	> 0		•				55712.09	60 16444	-0.00083
	2-Methyl-2-butene		-	_	0	0	'n	>	_	۰ د	، د	> 0	0	•			6926003	60 01777	0.00068
C ₅ H ₁₀ 3-Meth	3-Methyl-1-butene		0		0		'n	0	7	0 (7 0	-	- •	-	> 0	> <	29,97002	72,12054	0.00000
	ane	-	0	-	0	<u>-</u>	-	m	_	m	0	۰ د	- •	۰ ۵	۰ د	۰ د	72,03343	+0271.71	0.0013
C.H. mans-2.	rrans-2-Hexene		0	7	0	0	۲۱	7	C1	7	0	0	0	φ.	0	-	72.24636	25/57/	-0.00013
	rane_3-Hevene	_	0	2	0	0	7	7	7	7	0	0	0	0	0	0	72.24636	157577	00000-
	mil 1 montone			ı c	c	_	2	2	0	7	0	0	0	0	0	0	72.21854	72,29433	0.00105
CAH12 2-Medi	7-Methyl-1-hentene		٠,	> -	ı c	. c	ı er	ı -	_	_	0	0	0	0	0	0	72,37203	72,37206	0.0000
	2-Methyl-2-bentene		4 0		> <	۰ -	, (٠, ٠	_	,	0	c	0	0	0	72,13432	72.19173	0.00080
	3-Methyl-1-pentene	-	, c	<u>.</u> .	> 0		4 (4 (1 (1		Ċ	· c	C	0	72,10599	72.21038	0.00145
C ₆ H ₁₂ 4-Meth	4-Methyl-1-pentene		5	-	>	- (4		4	>	`	>	. i.	,	•				
C.H.: 3-Meth	3-Methyl-trans-2-	-	7	_	0	0	c	_	_		0	0	0	0	0	0	72.37203	72.33268	-0,00034
	ត្					,													
4-Meth	4-Methyl-trans-2-	-	0	7	0	Þ	'n	0	'n	Q	7	0	0	0	0	0	72.34745	72.31610	-0.00043
	ā	•	,		•		,	,	4	,	•	c	c	c	c	c	72 21854	72 25909	0.00056
	2-Ethyl-1-butene		0	0	7	-	7	7 6	> -	7 C	۰ د	> <	> <	> <		· c	72 31943	72 32543	0.00008
C ₆ H ₁₂ 2,3-Dii	2,3-Dimethyl-1-butene	_	0	φ.	C1 (.	n (0 0	- -	-	4 <	> 1*	o c	· c	• =	٠,	72.31796	72.30366	-0.00020
	3,3-Dimethyl-1-butene		0		5	- 0	n •	> 0	~ <		> <	, <				٠ .	72.49750	72.38450	-0.00156
	2,3-Dimethyl-2-butene		4	0	5 (۰.	ս -	> -	> -	> <	> <	> <		• •	• =	, ,	84.191.13	84.27084	0.00095
	tene	_	0		3			. .	- ر-	r -	۰, د	• =		· c			84.26369	84,30608	0.00050
C,H _L 5-Meth	5-Methyl-I-hexene	_	0		o c	- -	7 1	7 (7 -	- (n <	· c	· c	· c			84.52973	84,42112	-0.00129
-	trans-3-Methyl-3-hexene	_	7		5 (٠.	n (7 -		4 6	> t*	o C			· c		84.44880	84,49367	0.00053
	2,4-Dimethyl-1-pentene	-	0	o ·	7		· ·			> <	٦ -	•	• =				84.27012	84,47087	0.00238
	4,4-Dimethyl-1-pentene		٥ (-	- 0	o -	۔ د	۰, -	• •	۰,	- ح	· c		. 0	0	84.63062	84,54445	-0.00102
C ₂ H ₁₄ 2,4-Dii	2,4-Dimethyl-2-pentene		7	_	0	-	+	>	4	>	4	•					2000	01212	000
C.H., trans-4	trans-4,4-Dimethyl-2-	-	0	~1	0	>	4	0	61	0	0	m	ò	0	o ·	?	84.54076	84.54049	0,00000
						-									•			01077	000
C,H ₁₄ 2-Ethy	2-Ethyl-3-methyl-1-	-	0 .	0	7		'n	_	-		7	0	ō	0	0	>	84.47115	84.44910	-0.00055
	Durene 7 2 2 Trimodud 1					-		,	4	•	•	·	-	c	4	r	84 51274	84 51129	-0.0000
C,Hi Lifens	11111541131111	-	0	0	7		4	5	Ð	5	>	9	>	>	•	7			
C.H., 1-Octene	ine in	-	0	0	_	_	-	S	_	\$	0	0	oʻ	0	0	0	96.34883	96,41421	0.00068
	trans-2,2-Dimethyl-3-		c	r	•	0	Ψ	_	,	_	c	"	0	0	0	?	96.69846	96.68782	-0.0001
Carrie hexene		-	>	4	>		-	•	,										
C.H., 3-Ethy	3-Ethyl-2-methyl-1-	_	0	0	7	_	'n	7	_	7	7	0	0	0	0	0	96.63483	96.61113	-0.00025
	اد د	•				-													0,00
CsHin 2,4,4-Tr	2,4,4-Trimethyl-}-	_	0	0	2	-	4	_	0	0	0	4	0	0	0	0	96.61293	96.71684	0,0010
	2 4 4-Trimethyl-2-	•	í		c	0	v	-	-	c	c	r.	0	o	0	ņ	96.67590	96.65880	-0.00018
C ₈ H ₁₆ Dentene	2	o	7		>		•	•	-	•	•			, ,	. «		20777000	04045-001	יאטייט ט
	ene	_	0	-	0	-	_	7		7	0 (-	> 0	> <	> <	> c	144 07062	145.07163	0.00063
C12H24 1-Dod	1-Dodecene	-	0	-	0	-,		ο;		s :	0 0	.	> 0	> <	> <	, ,	103 61043	997 17 501	0.00055
	I-Hexadecene		٥	-		-	-	5	-	13		>	>	>		>	1000000	2014171	

	Exp. θ (°)			124.4 (1,1,5-hearniene C66-C6.9 (1,1,5-hearniene C,60-C6.9 (1,1,5-hearniene C,60-C6.9 (1,1,3-hearniene CC) (1,1,3-hearniene CC) (1,1,3-hearniene CC) (1,2-hearniene CC) (2,5-hearniene C6C-C6)		118.5 (2-methylpropene)	121 (2-methylpropene)	107 (propane)	112 (propane) 113.8 (butane) 110.8 (fsobutane)	111.0 (butane) 111.4 (isobutane)				110.8 (isobutane)		111.4 (isobutane)	111.4 (isobutane)	
	(aj. 6	118.36	113.84	123.46	118.19	116.31	121.85	108.44	110.49	110,49	109.50	109.44	109.44	110,67	110.76	111.27	111.27	107.50
	(c)			-	123.46	iA II												
	(o) -				118.36		116.31							i				
	θ (0)								69.51	15.69		70.56	70.56					72.50
m, msp².AO}.	$\stackrel{E_T}{(\text{eV})}$	0	-1.85836	-1.85836		0	} ·	0			0			-1.85836	0	0	-1,85836	
(atom – atc	. 'ar	1.07647	0.81549	0.81055		1.17300		1,15796	= 1	 	1.15796			0.81549	1.04887	1.04887	1.04887	
E_{T} is E_{T}	ڻ ⁻	0.75	1			0.75		0.75		u.	0.75			-	0.75	0.75	0.75	
vere used.	ర్	1	1	-		-		-	i					-	-	_	-	
ling angle v	ڻ ت	0.75	1	-		_	,	-			-			1	51.0	0.75	0.75	
the preced	С ₂ Atom 2	0.91771	0,81549	0.81549				-			1			0.81549	17716.0	0.91771	17716:0	
meters from	C ₂ Atem 1	0.85252	0,81549	0.80561		0.85252		0.86359			0.86359			0.81549	0.87495	0.87495	0.87495	
tion of $ heta_{_{\mathrm{c}}}$, the para	Atom 2 Hybridization Designation (Table 15.3.A)		. 24	22		ш		н			н			25	-		-	
n the calcula	E'carlembic Atom 2	-14,82575 C _c	.16.68411 C.	-ان(1484)		я		Œ			Œ			-16.68412 (°,	-14 82575 C _h	-14.82575 (',	-14.82575	
ental values [1].	Atom I Hybridization Designation (Table 15.3.A)	6	24			6		7		~	7			25	5	\$	8	
and experim	E Coulombie Atom 1	-15.95954	-16.68411 C	-16.88873 C,		-15,95955		-15.75493			-15.75493			-16.68412 (' _k	-15,55033	-15.55033 (' _h	-15.55033 C,	
alkenes	2c' Terminal Atoms (\alpha_0)	4.2895	4.7958	4,7539		3,4756		3.4252			3.4252			4,7958	4.1633	4.1633	4.7958	
ameters of	2c' Bund 2 (a ₀)	2.86175	2.86175	2,86175		2,04578		2.11106			2,09711			2,91547	2.11323	2.09711	2.90327	
d angle par	2c' Best i (a ₀)	2.11323	2 86175	2,53321		2,04578		2,11106			2,09711			2.91547	2,91547	2.91547	2.90327	
Table 15.20. The bond angle parameters of alkenes and experimental values [1]. In the calculation of θ_c , the parameters from the preceding angle were used. E_t is $E_t / (atom - atom, msp^2, AO)$	Atoms of Angle	$\angle HC_n C_r$ $(C_r(H)C_n = C_h)$	$(C_{c}(C_{c})C_{c} = C_{c})$	('ວ"ບ="ນ) ່ວ"ວ"ວ	ZHC.C.	$\angle HC_aH$ $(H_2C_a = C_bC_c)$	$\angle C_{k}C_{n}H$ $(H_{2}C_{n}=C_{k}C_{n})$	Methylene ZHC, H	*.7".7".7	4","	Methyl ZHC "H	ZC,C,C,	H, J, JZ	ر" در" در" 7."ر" در"	J. wt.	ZC_C,H iso C_	LC., C., C.	7C, C, C,

ALKYNES
$$(C_n H_{2n-2}, n = 3, 4, 5...\infty)$$

10

The straight and branched-chain alkynes, $C_n H_{2n-2}$, have at least one carbon-carbon triple bond comprising a functional group that is solved equivalently to the triple bond of acetylene. The triple bond may be bound to one or two carbon single bonds that substitute for the hydrogen 5 atoms of acetylene. Based on the energy matching of the mutually bound C, these C-C-bond MOs are defined as primary and secondary C-C functional groups, respectively, that are unique to alkynes. In addition, the corresponding terminal CH of a primary alkyne comprises a functional group that is solved equivalently to the methylyne group of acetylene as given in the Acetylene Molecule section.

The alkyl portion of the alkyne may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH₂), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In 15 addition, the C-C bonds within isopropyl ($(CH_3)_2 CH$) and t-butyl ($(CH_3)_3 C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkynes are equivalent to those in branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the 2s and 2p20 AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two C2sp3 HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. $E_T(atom-atom, msp^3.AO)$ of the $C \equiv C$ -bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of acetylene, $-3.13026 \ eV$, given by Eq. (14.342). $E_T(atom-atom, msp^3.AO)$ of each -alkyl-bond MO in 25 Eq. (15.52) is $-1.85836 \, eV$ or $-1.44915 \, eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, -0.92918 eV (Eq. (14.513), or methyl, $-0.72457 \, eV$ (Eq. (14.151)), groups, respectively. For the C-Cgroups each comprising a C single bond to $C \equiv C$, $E_T(atom-atom, msp^3.AO)$ is $-0.72457 \ eV$ based on the energy match between the $C2sp^3$ HOs for the mutually bound C of 30 the single and triple bonds. The parameter ω of each group is matched for oscillation in the transition state based on the group being primary or secondary.

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The symbols of the functional groups of alkynes are given in Table 15.21. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkynes are given in Tables 15.22, 15.23, and 15.24, respectively. The total energy of each alkyne given in Table 15.25 is calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.24 corresponding to functional-group composition of the molecule. The bond angle parameters of alkynes determined using Eqs. (15.79-15.108) are given in Table 15.26. Each C of the $C \equiv C$ group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene.

alkynes.	Je J	(i) (j = 1)	S(1)	(ii) H)	$C \sim H\left(CH_3\right)$	(H (CH.)	(1 H (i)	(a) (b) (b) (c) (a)	(A)		うとして	(a) (.) - (.)	(E) (3-1)
Table 15.21. The symbols of functional groups of alkynes. Functional Group	CC triple bond	C single bond to C ≤ C (1°)	C single band to $C \equiv C$ (2°)	CH (terminal)	CH, group	CH ₂ group	CH (alkyl)	CC band (n-C)	CC bond (iso-C)	CC bond (tert-C)	CC (iso to iso-C)	CC (t to t-C)	CC (t to iso-C)

Toble 15 22 T	The second section of the	1											
Parameter	Parameter Parameter	nd parameters of a	likynes and experit	nental values [1].	,				,				
	C ≡ C Group	Group	Croup	C-H (i)	$C-H(CH_3)$	$(C-H(CH_2))$	('-# (ii) Oroup	C'-C (a) Group	C-C (b)	C-C (e)	(c) (d)	(a) .) ~ .)	3-3
a (u ₀)	1.28714	1.99185	1.99185	1.48719	1 64920	1 67177	1				Thou,	dinoin	dnoir
c' (a.)	1 13457	1 41133	1 43122			771.10.1	(10/403	2.12499	2.12499	2.10725	2.12499	2,10725	2.1072
Rond Length	20101.F	1.411.50	1.41133	0.99572	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1 45164	1 45164
2c'(A)	1,20072	1.49369	1.49369	1.05383	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	>E9ES 1
					1 107	1,07							7
Exp. Bond Length	1.203 (acetylene) 1,208	1.450	1.450	1.060	(C - H propane)	(C – H propane)	1 122	[,532 (propere)	1.532	1.532	7:237	1,532	1.532
T	(2,4-hexadiyne)	(2,4-hexadiyne)	(2,4-hexadiyne)	(acetylene)	1.117 (C-H	L.117 (C-H	(isobutane)	(531 (6utane)	(propane) (.S31 (hitane)	(propane) 1.531	(propane) 1,531	(propane)	(propane 1.531
					butane)	butane)			(2)	Comme	(Outaine)	(outane)	(butane
n,c (a ₀)	0.60793	1.40557	1.40557	1.10466	1.27295	1.29569	1,29924	1.54616	1 54616	1 57750	264516	1 500000	
22	0.88143	0.70855	0.70855	5 699 0	0.63580	0.62160	20000	00000	olo: C:	04,24.1	01056.1	06/75"	(.52750
					ממריים, ח	6,00,00	0.65093	0.686(3)	0 68600	000000	000000	00000	

Table 15.23. The MO to HO intercept geometrical bond parameters of alkynes. L_T is L	trical bond	parameters of al.	Kynes. Ly 18 Ly	C_{τ} (arom – arom, msp. AO_{τ}).	- Cor den											
Bond	Atom	E.	E.	E.	E.	Final Total	Frankel	1,6.4	Ecutor (C2sp3)	$E(C2sp^3)$	ι,θ	θ	θ,	d,	ď,	
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C2sp³	(a ₀)	$(a_{\mathfrak{o}})$	(eV) Final	(eV) Final	©	©	©	(a _o)	(a,)	
RCCC -H	U	-1.56513	0	e	a	-153.18082	17116,0	0.83008	-16.39088	-16,20002	90.99	89.01	48.71	0.98144	0.01428	
# 3 J.)	ئ	-1.56513	-0.36229	0	0	-153.54311	17716.0	0.81213	-16.75317	-16,56231	137.17	42.83	65.25	0.53890	0.59562	
#'.7 ≡ '.7.7	ئ	-1,56513	0	c	0	-153.18082	17716,0	0.83008	-16.39088	-16,20002	137.91	42.09	66.24	0.51853	0,61599	
<i>y, v, v,</i>	ئن'	-0.36229	-0.92918	o	0	-152,90716	17716,0	0.84418	-16.11722	-15,92636	75.71	104,29	35.59	1.61974	0.20841	
$C-H$ (CH_3)	Ü	-0.92918	٥	c	0	-152,54487	177160	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708	
C-H (CH ₂)	J	-0.92918	-0,92918	0	0	-153,47406	17716.0	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933	
C-H (CH)	Ĵ	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1,42988	0.37326	. ,
$H_3C_4C_8H_2CH_2$ $(C-C_5(a))$	ر."	-0.92918	0	0	0	-152.54487	122160	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106	
$H_3C_3C_3H_2CH_2$ - $(C-C_3)$	C,	-0.92918	-0.92918	0	0	-153,47406	17716.0	0.81549	-16.68412	-16,49325	56,41	123.59	26.06	1,90890	0.45117	
$R - H_1(C_s(H_1C_s - R))H(H_2 - R)$ $(C - C_s(b))$	<i>C</i> ,	-0.92918	-0.92918	-0.92918	0 .	-154,40324	17716.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388	
$(R - H_1C_u(R' - H_2C_z)C_b(R'' - H_2C_z)CH_2 - (C - C'(c))$	ئ	-0.92918	-0.72457	-0.72457	-0.72457	-154,71860	17716'0	0.75889	-17.92866	-17,73779	48.21	131.79	21.74	1.95734	0.50570	
$lsoC_sC_s(H_1C_s - R^s)HCH_1 - (C - C_s(d))$	ڻ	-0.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388	
$ler(C_s(R^1-H_1C_s)C_h(R^1-H_2C_s)CH_1 - (C-C_1C_1)$	C,	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17,73779	50.04	129.96	22.66	1,94462	0.49298	,
$Ier(C_sC_s(H_1C_s-R^s)HCH_1-$ $(C-C_s(f))$	ť	-0.72457	-0.92918	-0.92918	S.	-154.19863	17716.0	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279	
$\kappa v C_{\mu}(R-H_1 C_{\mu}) C_{\mu}(R^{\mu}-H_1 C_{\mu}) C H_1 - C_{\mu}(R^{\mu}-H_1 C_{\mu}) C H_2 - C_{\mu}($	<i>'</i> 2	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	17716.0	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1,94462	0.49298	

	$C \equiv C$ Group	C-C (i) Group	C-C (ii) Group	C-H (i) Group	CH,	CH_2	C-H (ii)	C - C (a)	(4) C+C	(c) (c)	C-C (d)	(e) C-C	C-C (f)
-	3	_	-		3	2	1	1	1-	dionin —	oroup 1	Or Out	1
_	0	0	0	0	2	_	0	0	0	0	C	· c	· c
	0	0	0	0	0	0	0	0	0	0	0	0	, 0
	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
	_	_	-	-	_	_	1	-	-	-	-		-
	-	-		_		-	1	-	-	1	-	-	
	0.91771	0.91771	0.91771	0.91771	1771	0.91771	0.91771	0.91771	0.91771	0.91771	17716.0	0.91771	0.91771
	2	1	_	0	0	1	-	0	0	0	-	1	0
\dashv	9	2	2	1	1	1		2	7	2	2	2	2
	0	0	0	1	8	2	-	0	0	0	0	0	0
	0.5	0.5	0.5	0.75	52.0	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
	-		1	1	1			1	1	-	-		-
7	-182.53826	-31.29307	-31.29307	-40.62396	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
<u></u>	35.97770	9.64042	9.64042	13.66428	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
,	70.90876	7.85528	7.85528	13.65796	32.53914	21.06675	10,48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
-7	-35.45438	-3.92764	-3.92764	-6.82898	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
-	-16.20002	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
_	0	-0.72457	-0.72457	-3.130269	0	0	0	0	0	0	0	0	0
—	-16.20002	-13.91032	-13.91032	-11.50462	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
٠,	-94.90616	-31.63533	-31.63533	-31.63532	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
(eV)	-3.13026	-0.72457	-0.72457	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
ر.	-98.03637	-32.35994	-32.35994	-31.63537	-67.69450	-49.66493	-31.63537	-33,49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
-	20.0186	10.3988	17.5426	30.8370	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
	13.17659	6.84470	11.54682	20.29747	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
_	-0.23468	-0.16749	-0.21754	-0.28197	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
	0.27773	0.08989	0.08989 [9]	0.35532 Eq.	0.35532 Eq.	0.35532 Eq.	0.35532 Eq.	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
	-0.09581	-0.12255	-0.17260	-0.10430	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
6.	-98.02775	-32.48249	-32.53254	-31.73967	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	33.24376	-33.59732	-33.18712	-33.18712
-	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
-	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	0 - 0	0	0	0	0
<u>=</u>	10.21841	3.21271	3.26276	3.50634	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.24. The energy parameters (eV) of functional groups of alkynes.

111.4 (isobutane)

	Relative Error	v	-0.00085	0.00077
	Experimental	(eV)	29.40432	41.75705
,	Calculated Total Rond France	(eV)	29,42932	41.72765
	(J) C-C (e) C-C (f)		0 0	. 0
erimental values [7]		c	0	0
compared to the exn	C-C (b) $C-C$ (c) $C-C$ (d)		. 0	0
ergies of Table 15.24 compared to the	$^{\prime\prime}H$ (ii) $^{\prime\prime}C$ – $^{\prime\prime}C$ (a) $^{\prime\prime}C$	0	0 1	0 4
nposition and the en	CH ₂	0	-	0 9
functional group co	CH (i) CH ₃	-		7 -
calculated using the	.) <u>(ii)</u>	0	0.	70
energies of alkynes	.) .) (i)			
Name		Propyne	1-Butyne 2-Butyne	1-Nonyne
Formula		CH,	בָּבְּי בַּבְּי	C,H _{Ic}

ALKYL FLUORIDES
$$(C_n H_{2n+2-m} F_m, n=1,2,3,4,5... \infty m=1,2,3... \infty)$$

The branched-chain alkyl fluorides, $C_nH_{2n+2-m}F_m$, may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein at least one H is replaced by a fluorine. The C-F bond comprises a functional group for each case of F replacing a H of methane in the series $H_{4-m}C-F_m$, m=1,2,3,4, and F replacing a H of an alkane. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2CH)$ and t-butyl $((CH_3)_3C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the C-F functional groups comprises the hybridization of the 2s and 2p AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the F AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl fluorides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)), and the F AO has an energy of $E(F) = -17.42282 \, eV$. To meet the equipotential condition of the union of the C-F H_2 -20 type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the C-F-bond MO given by Eqs. (15.68) and (15.70) is

$$c_2\left(C2sp^3HO\ to\ F\right) = \frac{E\left(C,2sp^3\right)}{E\left(F\right)}c_2\left(C2sp^3HO\right) = \frac{-14.63489\ eV}{-17.42282\ eV}\left(0.91771\right) = 0.77087 \quad (15.110)$$

 $E_T(atom-atom,msp^3.AO)$ of the C-F-bond MO in Eq. (15.52) based on the charge donation from F to the MO is determined by the linear combination that results in a energy that is a minimum which does not exceed the energy of the AO of the F atom to which it is energy matched.

The symbols of the functional groups of branched-chain alkyl fluorides are given in Table 15.27. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl fluorides are

given in Tables 15.28, 15.29, and 15.30, respectively. The total energy of each branched-chain alkyl fluoride given in Table 15.31 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.30 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). In the case of trifluoromethane, E_{mag} is positive since the term due to the fluorine atoms cancels that of the CH group. The C-C bonds to the CHF group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CF group (no H bonds to C) were each treated as a tert-butyl C-C. E_{mag} was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl fluorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.110) are given in Table 15.32.

Table 15.27. The symbols of functional groups of branched-chain alkyl fluorides.

Functional Group	Group Symbol
CF of $CF_m H_{4-m}$	C-F (i)
CF of $C_n H_{2n+2-m} F_m$	C-F (ii)
CH ₃ group	$C-H$ $\left(CH_{3}\right)$
CH ₂ group	$C-H$ $\left(CH_{2}\right)$
СН	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

	(E)	Group	2.10725	1.45164	1.53635	1.532	(propane)].53]	(butane)	1.52750	0.68888
	(C-C)	Group	2.10725	1.45164	1.53635	1.532	(propane)	1.531	(butane)	1.52750	0.68888
	(g)	Group	2.12499	1.45744	1.54280	1.532	(propane)	1.531	(butane)	1.54616	0.68600
	(©) ()-()	Group	2.10725	1,45164	1.53635	1.532	(bropane)	1,531	(butane)	1.52750	0.68888
	ر (<u>a</u>)	Group	2.12499	1.45744	1.54280	1.532	(propane)	1.531	(butane)	1.54616	0.68600
	(; -(, (a)	Group	2.12499	1.45744	1.54280	1,532	(propane)	1.531	(butane)	1,54616	0.68600
ital values i j.	C-H	Group	1.67465	1.05661	1.11827		1.122	(isobutane)		1.29924	0.63095
air vi intollides and experimental values in	(H.) H - J	Group	1.67122	1.05553	1,11713	1.107	(C - H propane)	1.117	(C-H butane)	1.29569	0.63159
CICO-CISCIII AINAI 110	(HJ)H-J	Group	1.64920	1.04856	1.10974	1.107	(C-H propane)	1.117	(C-H butane)	1.27295	0.63580
d Jalanicies of Ola	C-F (ii)	Group	1.72139	1,31202	1,38858		1.382	(methyl fluoride)		1.11435	0.76219
l able 13.26. The geometrical point parameters of oranoneo-citam	(I) C-E (I)	Group	1.72139	1.31202	1.38858		1.382	methyl fluoride)		1.11435	0.76219
1 able 13.20.	Parameter		a (a _o)	$c'(a_0)$	Bond Length 2c* (A)	Evn Rond	Lap. Cons	\(\frac{1}{3}\)	(¥)	h,c (a_0)	a

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ters of branched-chain alkyl fluorides. R,R',R" are H or alkyl groups.	
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Bond	Atom	E ₇ (eV) Bond I	E_T (eV) Bond 2	E ₇ (eV) Bond 3	\mathcal{E}_T (eV) Bond 4	Final Total Energy ("2sp" (eV)	(a_0)	$\begin{pmatrix} r_{inst} \\ a_0 \end{pmatrix}$	Economis (eV) Final	E(C2sp³) (eV) Final	(°)	(°)	(6)	$\begin{pmatrix} a_1 \\ a_0 \end{pmatrix}$	$\begin{pmatrix} a_1 \\ a_0 \end{pmatrix}$
$H_{4-m}C_{,i} - F_{m}$ $(C_{,i} - F_{ij})$	ن	-1.34946	0	0	0	-152,96515	0.91771	0,84115	-16.17521	-15,98435	100.77	79.23	47.86	1.15488	0.15714
$H_{\lambda-m}C_{\nu} - F_{m}$ $(C_{\mu} - F (1))$	i L	-1,34946	0	0	0		0.78069	0.84115	-16.17521		100.77	79.23	47.86	1.15488	0.15714
$-H_2(k',F)$ $(C'_n-F(i))$	"ن	-1.34946	-0.92918	0	0	-153,89433	0.91771	0.79546	-17.10440	-16.91353	97.02	82.98	45.11	1.21483	0.09718
$-H_{\mathcal{L},\mathcal{K}',\mathcal{F}}$ $(C_{-F}(ij))$	وو	-1.34946	0	Q	0		0.78069	0.84115	-16.17521		100.77	79.23	47.86	1.15488	0.15714
$C-H$ (CH_3)	į.	-0.92918	°	0	0	-152,54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$(C-H(CH_2))$	ر	-0.92918	-0,92918	0	0	-153.47406	17716.0	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
C-H (C.H)	Ü	-0.92918	-0.92918	-0.92918	0	-154,40324	17716.0	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_*C_*H_3CH_2$	ບ້	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$(G_{\mu_1}^{C}C_{\mu_2}^{C}H_2^{\mu_2}-(G_{\mu_1}^{C}G_{\mu_2}^{C}G_{\mu_2}^{C}G_{\mu_3}^$	υ ^t	-0.92918	-0.92918	0	0	-153,47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R - H_2^*C_s(H_2^*C_s - R^*)HCH_2 - C(C - C(D))$	ぴ	-0.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.77247	-17,61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2C_a(R' - H_2C_a)C_b(R' - H_2C_c)CH_2 - (C - C'(c))$	ť	-0.92918	-0.72457	-0.72457	-0.72457	-154,71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_{\mu}C_{\mu}(H_{\underline{a}}C_{\mu}-R^{\prime})HCH_{\underline{a}}$ $(C-C^{\prime}(d))$	౮	-0.92918	-0,92918	-0.92918	0	-154,40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	791167	0.51388
$(R' - H_2C_4)C_6(R' - H_2C_5)C_{H_2} - (C - C'(e))$	ئ	-0 72457	-0,72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$terC_{i}C_{i}(H_{1}C_{i}-R^{i})HCH_{1}-$ $(C-C_{i}(f))$	ئن	-0.72457	-0.92918	-0.92918	-0	-154,19863	0.91771	0.78155	-17.40869	-17,21783	52.78	127.22	24.04	1.92443	0.47279
$ixoC_{a}(R-H_{2}C_{d})C_{b}(R^{n}-H_{2}C_{c})CH_{2} - (C-C_{c}(f))$	ڻ	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	17710	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1,94462	0.49298

Parameters C-F C	<u>(- F</u>) H. H-D	H.)	H.)	H-J	(a)	C-C (b)	() (c)	(g) (J-1)	(e)	(f)
	(i) Group	(ii) Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
п,	-	-	-	2	-	-	-	-	_	 -	-
11,2	o	0	2		0	0	0	0	0	0	0
11,	0	0	0	0	0	0	0	0	0	0	0
· .	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ر	- ;	_	-		-	-	-	-	_	-	1
5	_	-		1	-	1	-	-	-	-	1
5	0.77087	0.77087	0.91771	17716.0	17716.0	0,91771	0.91771	0.91771	17716.0	0.91771	17716.0
ິ້ນ	0	0	0	_	-	0	0	0	-		0
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.,	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0,5	0.5	0.5	0.5
ٿ.	-	-	1		_	_		-	_	-	-
V, (eV)	-32.02108	-32,02108	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	10.37015	10.37015	38,92728	25.78002	12.87680	9,33352	9.33352	9.37273	9,33352	9.37273	9.37273
T' (aV)	9.30097	9.30097	32,53914	21.06675	10,48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V,, (eV)	-4.65048	-4.65048	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3,45250
E(10 ta) (eV)	-14.63489	-14,63489	-15,56407	-15.36407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-13,35946
$\Delta E_{\mu_{\lambda MO}}(.o.m)$ (eV)	0	0	0	0	0	0	0	0	0	0	0
$E_T(\omega m)$ (eV)	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15,56407	-15.35946	-15.56407	-15.35946	-15,35946
$E_{\tau}(n_{zM})$ $(a\dot{V})$	-31.63534	-31.63534	-67.69451	-49.66493	-31,63533	-31,63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom - atom, mxp^3, AO)$ (eV)	-2.69892	-2.69892	0	0	0	-1.85836	-1.85836	-1,44915	-1,85836	-1.44915	-1.44915
$E_T(uv)$ (eV)	-34.33429	-34.33429	-67.69450	-49.66493	-31,63537	-33.49373	-33.49373	-33,08452	-33.49373	-33.08452	-33.08452
$\omega \left(10^{15} rad l.s\right)$	24.8506	12,9435	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9,43699	9.55643	9.55643
E_{K} (aV)	16.35707	8.51966	16.40846	15.97831	15.91299	621159	6.21159	10,19220	621159	6.29021	6.29021
\widetilde{E}_{p} (eV)	-0.27472	-0.19826	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
\widetilde{E}_{Kirb} (eV)	0.13849 [10]	0.10911	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944	0.12312 [2]	0.12312	0.12312
$\vec{E}_{\alpha c}$ (eV)	-0,20547	-0.14371	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{m_{tot}}(eV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(\sigma_{mip} (eV))$	-34.53976	-34.47800	-67.92207	-49,80996	-31,70737	-33,59732	-33,49373	-33,24376	-33,59732	-33.18712	-33.18712
Eumal (c. 40 110) (UV)	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489
Eumot (c. 10 111) (eV)	0	0	-13.59844	-13,59844	-13.59844	0	0	0	0	0	0
$E_{D}(Grup)(eV)$	5.26998	5,20822	12.49186	7.83016	3,32601	4,32754	4.29921	3,97398	4.17951	3.62128	3.91734

Table 15.31. The total bond energies of branched-chain alkyl fluorides calculated using the functional group composition and the energies of Table 15.30 compared to the experimental values [2]. The magnetic energy E_

weighted:	weighted sum of the $E_{D}(i_{mm})$ (eV) values based on composition is given b	alues based on cor	mposition is give	en by (13.58).	,											
Formula	Name	C-F(i) $C-F(ii)$	C-F (ii)	CH ₃	CH,	CH	C – C (a)	C-C (b)	(a) D-D	$C-C \ (a) C-C \ (b) C-C \ (c) C-C \ (d) C-C \ (d) C-C \ (d)$	(a) D-D	() 2-2	E mog	Calculated Total Bond Energy (eV)	Experimental Relative Error Total Bond Energy (eV)	Relative Error
F.	Tetrafluoromethane	4	٥	٥	o	0	0	0	0	0	0	0	0	1	21.016	-0.00303
CHF,	Trifluoromethate	ъ.	0	o	0	-	0	0	0	0	0	0	•		19.362	0.00405
CH ₂ F ₂	Difluoromethane	2	0	0	_	0	0	0	0	0	0	0	0		18.280	-0.00496
C,H,F	1-Fluoropropane	0	_	-	7	0	7	0	0	0	0	0	7		41.885	0.00041
C.H.F	2-Filomonroome	-	_	,	•	-	c	,	•		c	-	-		41 062	CIUOVO

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	Exp. <i>θ</i>		108.8 (fluoroform)		110.3 (1,2-difluoroethane)	111.0 (1,1-difluomethane)	107 (propane)	112 (propane) 113.8 (butane) 110.8 (fsobutane)	111.0 (butane) 111.4 (isobutane)				110.8 (isobutane)		111.4 (isobutane)	111.4 (isobutane)	
	E 0 E	()	110.53	110,38	111.53	110.83	108.44	110.49	110,49	109.50	109.44	109.44	110.67	110.76	111.27	111.27	107.50
·	0,0																
n,msp³.A	θ ₁ (C))															
т – агоп	φ̂ (0)							69.51	69.51		70.56	70,56					72.50
E_T is $E_T(ato)$	E_T (eV)		-1,44915	0	-1.85836	0	0			0			-1.85836	0	0	-1.85836	
were used	25		6.84115	0.98172	0.79318	1.04887	1.15796			1,15796			0.81549	1.04887	1.04887	1.04887	
ling angle	5			0.75	-	0.75	0.75			0.75			-	0.75	0.75	0.75	
n the prece	5		-	-	-	-	_			1			-	_	-	-	
meters fron	5		1	0.75	-	0.75	-			1			-	27.0	0.75	0.75	
of $\theta_{\rm r}$, the para	C ₂ Alon 2		0.84115	0,78092 (Eq. (15.64))	0.77087 (Eq. (15.110))	0,91771	1			1			0.8/549	0.91771	0.91771	0.91771	
the calculation	С ₂ Люн 1		0.84115	0.79546	0.81549	0.87495	0.86359			0.86359			0.81549	0.87495	0.87495	0.87495	
Table 15.32. The bond angle parameters of branched-chain alkyl fluorides and experimental values [1]. In the calculation of θ_r , the parameters from the preceding angle were used. E_T is $E_T(anom - anom, msp^3 AO)$	Atom 2 Hybridization Designation	(Table 15.3.A)	12	Ŀ	<u>I</u> I.				7				. 25	-	13	1	,
nd experime	Econtrastre Atom 2		-16.17521 F	-17.42282 F	-17.42282 F	-14.82575 C,	н			Н			-16,68412	-14.82575 (',	-14.82575 (',	-14,82575 C,	
ı alkyl fluorides a	Atom 1 Hybridization Designation	(Table 15.3.A)	12	31	25	S	7			7			25	S	5	s	
nched-chair	Erakombe Akmi l		-16.17521 F	-17.10440 C.	-16.68412 C,	-15.55033 C,	-15.75493			-15,75493			-16 68412	-15.55033 C,	-15.55033 C,	-15.55033 C' ₆	
eters of bra		(00)	4,3128	3.8987	4.5826	4.1633	3 4252			3.4252			4.7958	4.1633	4,1633	4.7958	
ngle param	2c' Bend 2 (a _a)		2.62403	2.62403	2.62403	2,11106	2.11106			2.09711			2 91547	211323	111607	2,90327	
The bond a	2c' Bond i (a _b)		2,62403	2.11106	2.91547	2,91547	2,11106			2.09711			2.91547	291547	2.91547	2,90327	
Table 15.32.	Atoms of Angle		$\angle FC_{\mu}F$ $(C_{\mu}-F_{\mu}(i))$	$\angle HC_FF$ (C, $-F$ (i)	$\begin{array}{c} ZC_{s}C_{s}F\\ (C_{s}-F\\ (ii)) \end{array}$	$\angle C_s C_s H$ $(C_s - F$ (ii))	Melivkne ZHC, H	'כנ"כ".	H",J",37	Methy! ZHC, H	,""	H',),",),"	".) ⁶⁸ ".)".)7	ZC,C,H iso C,	ZC,C,H in C,	ZC,C,C, test C,	3.337

ALKYL CHLORIDES
$$(C_n H_{2n+2-m} Cl_m, n = 1, 2, 3, 4, 5... \infty m = 1, 2, 3... \infty)$$

The branched-chain alkyl chlorides, $C_n H_{2n+2-m} Cl_m$, may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein at least one H is replaced by a chlorine. The C-Cl bond comprises a functional group for each case of Cl replacing a H of methane for the series $H_{4-m}C-Cl_m$, m=1,2,3, with the C-Cl bond of CCl_4 comprising another functional group due to the limitation of the minimum energy of Cl matched to that of the $C2sp^3$ HO. In addition, the C-Cl bond due to Cl replacing a H of an alkane is a function group. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the C-Cl functional groups comprises the hybridization of the 2s and 2p AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the Cl AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl chlorides, the energy of chorine is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is one and the energy metabing condition is determined by the C parameter. Then

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20 (15.52) is one, and the energy matching condition is determined by the C_2 parameter. Then, $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489~eV~$ (Eq. (15.25)), and the Cl~ AO has an energy of $E\left(Cl\right)=-12.96764~eV~$. To meet the equipotential condition of the union of the C-Cl~ H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.52) for the 25 C-Cl-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ Cl\right) = \frac{E(Cl)}{E(C,2sp^3)}c_2\left(C2sp^3HO\right) = \frac{-12.96764\ eV}{-14.63489\ eV}(0.91771) = 0.81317\ (15.110)$$

The valence energy of the carbon 2p is $-11.2603 \, eV$ and that of the Cl AO is $-12.96764 \, eV$. The energy difference is more than that of $2E_T \left(C-C,2sp^3\right)$ given by Eq. (14.151) for a single

bond. Thus, $E_r(atom-atom,msp^3.AO)$ of the C-Cl-bond MO in Eq. (15.52) due to the charge donation from the C and Cl atoms to the MO is -1.44915~eV based on the energy match between the $C2sp^3$ HO and the Cl AO corresponding to the energy contributions equivalent to those of methyl groups, -0.72457~eV (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl chlorides are given in Table 15.33. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl chlorides are given in Tables 15.34, 15.35, and 15.36, respectively. The total energy of each branched-chain alkyl chloride given in Table 15.37 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.36 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that was subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The C-C bonds to the CHCl group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CCl group (no H bonds to C) were each treated as a tert-butyl C-C. E_{mag} was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl chlorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.111) are given in Table 15.38.

Table 15.33. The symbols of functional groups of branched-chain alkyl chlorides.

14010 13.33. 140 5/140045	2 2 3 3 3 3 4 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
Functional Group	Group Symbol
CCl of $CCl_m H_{4-m}$	C-Cl (i)
CCl of CCl ₄	C-Cl (ii)
CCl of $C_n H_{2n+2-m} Cl_m$	C-Cl (iii)
CH₃ group	$C-H\left(CH_{3}\right)$
CH₂ group	$C-H$ (CH_2)
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	'C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Group Group Group	2.12499 2.10725 2.10725	1.45744 1.45164 1.45164	1.53635 1.53635	1.532	(propane) (propane) (propane)	1,531	(butane) (butane) (butane)	1.54616 1.52750 1.52750	
C-C (c) Group	2.10725	1.45164	(.53635	1,532	(propane)	1.531	(butane)	1.52750	
Croup Group	2.12499	1,45744	1.54280	1.532	(propane)	153.	(butane)	1.54616	
C – C (a) Group	2.12499	1.45744	1.54280	1.532	(propane)	1.531	(butane)	1.54616	
C'-H Group	1.67465	1,05661	1.11827		1.122	(isobutane)		1,29924	
$C - H \left(CH_2 \right)$ Group	1.67122	1.05553	1.11713	1.107	(C-H propane)	1.117	(C-H butane)	1.29569	
$(-H(CH_3)$ Group	1.64920	1.04856	1.10974	1.107	(C-H propane)	1.117	(C-H butane)	1.27295	
C – CI (iii) Group	2,32621	1.69136	1.79005	1 802	(cthyl chioride)	1.790	(1.2-dichlorocthane)	1.59705	
Parameter C-CI (i) C-CI (ii) C-CI (iii) Group Group	2.37026	1.70729	1.80692		1.767	(carbon tetrachloride)		1.64416	
C - C/ (i)	2,32621	1,69136	1.79005		1.785	(methyl chloride)	Ì	1,59705	i
Parameter	a (a _n)	c. (a,)	Bond Length 2c' (A)	0	Lxp. bond	100	₹	b, c (a,)	

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Bond	Атоп	β., (eV) Bond I	Ε _τ (eV) Bond 2	/i, (eV) Bond 3	E ₇ (eV) Bond 4	Final Total Energy (7.25p ³	Can)	$(a_n)^{r_{perf}}$	Erculeup (eV) Final	$E(C2sp^3)$ (eV) Final	. _θ (ο)	θ ()	θ	$\begin{pmatrix} d_1 \\ (a_a \end{pmatrix}$	$\begin{pmatrix} d_2 \\ (\sigma_0 \end{pmatrix}$
$H_{4-n}(', -(1/n), m = 1, 2, 3, 1)$	نّ	-0.72457	0	0	0	-152.34026	0,91771	0.87495	-15.55033	-15.35946	69.62	110.38	30,90	1.99599	0.30463
$H_{t,n}(x, -t', m = 1, 2, 3, t', -t', (t', -t', t'))$	5	-0,72457	٥	0	a		1.05158	0.87495	-15.55033		69.62	110.38	30.90	1.99599	0.30463
(',''') (',''-(''))	ن	-0.46459	G	0	0	-152.08028	0.91771	0.88983	-15.29034	-15.09948	86.98	113.02	29.87	2.05530	0.34801
(',"C' ₁ ((C', ~('' (ii))	5	-0.46459	9	D	0		1.05158	0.88983	-15.29034		66.98	113.02	29.87	2.05530	0.34801
-H ₂ C, C, a - C! (C, a - C! (iii))	ئ	-0.72457	-0.92918	0	0	-153.26945	17716.0	0.82562	-16.47951	-16.28864	81.8	116.82	27.48	2.06384	0.37248
-H ₂ C,C, -C! -H ₂ C,C', -C!	٦	-0.72457	0	0	0		1.05158	0.87495	-15.55033		69.62	110.38	30.90	1.99599	0.30463
C-H (CH,)		-0.92918	0	0	0	-152.54487	17716.0	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1,23564	0.18708
C-H (CH,)	; ;	-0,92918	-0.92918	0	0	-153.47406	17716.0	0.81549	-16,68412	-16,49325	68.47	111.53	35.84	1,35486	0.29933
(H (C.H)	ر	-0,92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17,61330	-17,42244	61.10	118.90	31.37	1.42988	0.37326
$H_1^{C}(C, H_2^{-1}H_2^{-1})$	υ*	-0.92918	6	0	0	-152.54487	0.91771	0.86359	-15.75493	-15,56407	63.82	116.18	30.08	1.83879	0.38106
$H_1^{C}(C, H_2^{C}(H_2^{-m}))$	نٔ	-0.92918	-0.92918	0	0	-153.47406	0,91771	0.81549	-16.68412	-16,49325	36.41	123.59	26.06	1,90890	0,45117
$R - H_2(J_s(H_2C_s - R)HCH_2 - (C - C (b))$	ڻ	-0,92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	791267	0.51388
$R = H_2(', (R' - H_2C_J)C_k(R'' - H_2C_c)CH_2 - (C - C', C))$	ť	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17,92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$lsoC_{*}C_{*}(H_{2}C_{*}-R)HCH_{2}-$ (C'-(' (d))	نځ	-0.92918	-0,92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$ter(C_n(R^n - H_2C_s)C_s(R^n - H_2C_s)CH_2 - C(C^n - C(s))$	υ [*]	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
(C-C, G)	ť	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$lxoC_{\mu}(R-H_2C_{\mu})C_{\lambda}(R^{\mu}-H_2C_{\mu})CH_2-(C^{\mu}-C^{\mu})CH_2$	ť.	-0,72457	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Parameters	C-Cl (i) Group	C-C	C-C(iii) Group	C'H ₃ Group	CH ₂ Group	C−H Group	C-C (a) Group	C-C (b) Group	(c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
"	_			3	2	_	-	-	-	_	-	_
n,	0	0	, 0	2	-	0	0	0	0	o	0	0
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	0.5	0.5	0.5	0.75	0.75	0.75	0,5	0.5	0.5	0.5	0.5	0.5
ر.ً	0.81317	0.81317	0.81317	1	_	_	_	1	_	_	-	-
<i>c</i> ₁	-	_			1	1	_		-	-	_	-
د.	-	_	-	0.91771	0.91771	17716'0	0.91771	0.91771	0.91771	0.91771	171160	0,91771
6,3	-	-	-	0	-	-	0	0	0	-	-	0
c,	2	2	2	_		-	2	2	2	2	2	2
رَّ	0	0	0	m	2	-	. 0	0	0	0	0	0
اله	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	5.0	0.5	0.5	0.5
°°,	0.81317	0.81317	0.81317	-	_	1	1		_	-	1	-
V, (eV)	-29,68411	-28.95265	-29.68411	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	8.04432	7.96922	8.04432	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	6.38036	6.10748	6.38036	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V, (eV)	-3.19018	-3.05374	-3.19018	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
El.m na) (eV)	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15,35946	-15,35946
$\Delta E_{H_2M_2}(w uo) (aV)$	-1.44915	-0.92918	-1.44915	0	0	0	0	0	0	0	0	0
$E_T(\omega)$ no (eV)	-13.18574	-13,70571	-13.18574	-15,56407	-15,56407	-14,63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-15.35946
$E_T[n_2 so] (eV)$	-31.63536	-31.63540	-31,63536	-67,69451	-49.66493	-31,63533	-31.63537	-31,63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{\tau}(atom - atom, msp^{2}.AO)$ (cV)	-1.44915	-0.92918	-1.44915	0	0	0	-1.85836	-1,85836	-1.44915	-1.85836	-1.44915	-1.44915
E_ (10) (eV)	-33.08452	-32,56455	-33.08452	-67.69450	-49,66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega \left(10^{15} rad/s\right)$	7.42995	7.22380	13.0612	24.9286	24.2751	24,1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_{\mathbf{k}}$ (eV)	4.89052	4.75483	8.59708	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6,21159	6.29021	6.29021
E_{p} (eV)	-0.14475	-0.14048	-0.19191	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{\mathrm{Krub}}$ (eV)	0.08059 [12]	0.08059	0,091[3 [13]	0.35532 (Eq. (13.458))	0,35532 (Eq. (13,458))	0.35532 (Eq. (13.458))	0.12312	0.17978	0.09944	0.12312	0.12512	0.12312
$E_{ac}(eV)$	-0.10445	-0.10019	-0.14635	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Ent. (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T^{(c)}(eV)$	-33,18897	-32.66473	-33.23086	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E mind (c1.10 110) (cV)	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
E antre (c. 10 110) (cV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
Entiman (eV)	3.77116	3.39496	3.96108	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.37. The total bond energies of branched-chain alkyl chlorides calculated using the functional group composition and the energies of Table 15.36 compared to the experimental values [2]. The magnetic energy E_{ac} that is subtracted from the weighted sum of the E_a [car] (et') values based on composition is given by (15.58).

Formula Name C-Cf (ii) C-Cf (iii) C-C (ii

1																				
Relative Error		0.00123	0.00217	0.00499	0.00299	-0.00138	-0.00112	-0.00028	-0.00044	-0.00104	-0.00085	-0.00037	0,00034	-0.00069	-0.00037	0.00002	-0.00038	0.00007	0.00009	010000
Experiment al Total Bond	Energy (eV)	13.448	14.523	15.450	16,312	28.571	40.723	40.858	52.903	52.972	52.953	53.191	65.061	65.111	65.344	65.167	77.313	101.564	150,202	373 576
Calculated Total Bond	Energy (ev)	13.43181	14.49146	15.37248	16,26302	28.61064	40.76834	40.86923	52.92604	52.02693	52.99860	53.21057	65.08379	65.15630	65.36827	65.16582	77.34233	101.55684	150.87640	772 12201
E MES		7	-	0	0	0	0	0	0	0	0	-	0	0	-	0	0	0	0	_
C-C (i)		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	c
(H (H) ('-('(a) ('-('(b) ('-('(a) ('-('(a) ('-('(a) ('-('(a) ('-('(a) ('-('(a) ('-('(a) (')))))))))		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C-C(d)		٠ د	0	0	0	0	0	0	0	0	0	0	0	0 (o		0	0 '	0	0
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C-Cl (III)	4	c		0	. –						_		_			L	-			
C-C1(i) C-C1(ii) C-C1(iii)	0	0	0	0	0					0	0	0	0	0	c		0	0	0	
C-C1 (i)	0	'n	7		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Мате	Tetrachioromethane	Trichforomethane	Dichloromethane	Chloromethane	Chloroethane	1-Chloropropane	2-Chloropropane	1-Chlorobutpane	2-Chlorobutane	1-Chloro-2-methylpropane	2-Chloro-2-methylpropane	1-Chloropentane	I-Chloro-3-methylbutane	2-Chloro-2-methylbutane	2-Chloro-3-methylbutane	2-Chlorohexane	1-Chlorooctane	I-Chlorododecane	I-Chlorooctadecane	
Formula	Γ		_	_	Ĭ		• •	-	7	CHO	C,H,Cl	CHIC	_	r.ı	C,H,ICI 2	ы		_	_	

Exp. θ	1120 (dichloromethane) 111.3 (chloroform)		(192.) (AIC_H edyl chloride) 109.8 (AIC_H edyl chloride)		(edy) falloride) (1,1-dichlorochano) (1,2-dichlorochano) (1,2-dichlorochano) (1,1-dichlorochano) (1,1-dichlorochano) (1,0-dichlorochano)	110.6 (cthyl ctiloride)	107 (propane)	112 (propane) 113.8 (butene) 110.8 (festbutane)	111.0 (butane) 111.4 (jschutane)				IIO.8 (isobulanc)		111.4 (isabutanc)	III.4 (isobutane)	
© 6 gi		111.46	05.601	109 44	109.61 CL	110.83	108.44	110.49	110.49	05 601	109.44	109.41	110.67	110.76	111 27	111.27	107.50
(3)	+			-													
9 0	 										\dashv				_		
1 0° 5°	-			70,56				69.51	69.51		70.56	70.56					72.50
E ₇ (eV)	-0.92918	c	0		40,92918	ij	0			u			-1.85836	0	c	-1.85836	
25 ct 4c	0.91771	5,77000.1	1.15796		0.86359	1,04887	1.15796			1.15796			0.81549	1.04887	1,04887	1.04887	
c c		57:0	67.0		_	0.75	0,75			0.75			-	0.75	67.0	0.75	S.
C.	0,81317 (Eq. (15.111))	0,95310 (පිඅ. (15.65))	_		0,81317 (Eq. (15.111))	-	-	,		_			-	-	_	_	ŀ
C ₁	-	0.75	-			67.0	_			-				0.75	0.75	0,75	
C. Man 2	0,91771	17719.0	_		0.86359	0.91771	_			-			0.X1549	1771	0.91771	0.91771	
C, Man J	17716.0	0.83680	0.86359		ต.พกรรภ	0.87495	0,86359			0.86359			0.81549	0.87495	0,87495	0.87495	
Atom 2 (Ity bridization Designation	(Table 15.3.A)	១	=		១	_	Ξ			Ξ			દ		1	-	
Ereshutha Atom 2	-14.82575 Cl	-12.96764 (')	=		-12,96764	-14 K2575	=			=			-16.68412 C',	-14.82575	-14.82575	-14,82575 C,	
Atoni I Atoni I Urbridization Designation	(Table 15.3.A)	9	1		,	'n	7			7			æ	•6	s.	20	
Erodenta	.14x575	-16.27490	-15.75493		-15.75.493	-15.55m3 (*,	-15,75497			-15.75493			-16.08412 C.	".) ::::::::::::::::::::::::::::::::::::	-15.55033 (*,	-15,58033	
Ze' Tamarel Tomare	5.3K89	1965.4	3.4252		5.1539	4,1633	3,1252			3.1252			4.7958	4 1633	4.1635	4.795k	
2c' Bond 2 (a,)	3,34271	3,38271	2.09711		3,38271	2.11106	2,11106			3.19711			191547	211333	2.09711	72,707,27	
2c' Bond (a,)	3,3827.1	2,11106	2.09711		2,915.47	1,91547	2,11106			2.09711			2.91547	2.91547	2,91547	2.90327	
Since 15.35. The bond angig parameters of branches and experimental varies 13.01. The bond angig parameters of branches and experimental varies 13.01. Trained Trained	(C, -('' ('))	((<u> </u> (<u> </u>)))	ZHC,H ZHC,H	ZC,C,H, ((C, -C'' (iii))	((; -c.t (iii))	((', -(') (ii))	Wednest ALC., H	3,55.7	H*5".)7	Vicing ZHC, H	`.)".)7	H,'),')\	۳۰ ر." ۲۲.۴۲."د.	H'.)",7	H,7,72	, D tot	75,5,77

ALKYL BROMIDES (
$$C_n H_{2n+2-m} Br_m$$
, $n = 1, 2, 3, 4, 5... \infty$ $m = 1, 2, 3... \infty$)

The branched-chain alkyl bromides, $C_n H_{2n+2-m} Br_m$, may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein at least one H is replaced by a bromine. The C-Br bond comprises a functional group for each case of Br replacing a H of methane for the series $H_{4-m}C-Br_m$, m=1,2,3, with the C-Br bond of CBr_4 comprising another functional group due to the limitation of the minimum energy of Br matched to that of the $C2sp^3$ HO. In addition, the C-Br bond due to Br replacing a H of an alkane is a function group. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2CH)$ and t-butyl $((CH_3)_3C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the C-Br functional groups comprises the hybridization of the 2s and 2p shells of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ hybridized orbital (HO) and the Br AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl bromides, the energy of bromine is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. Then, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)), and the Br AO has an energy of $E(Br) = -11.81381 \, eV$. To meet the equipotential condition of the union of the C-Br H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.52) for the C-Br-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ Br\right) = \frac{E(Br)}{E\left(C,2sp^3\right)}c_2\left(C2sp^3HO\right) = \frac{-11.81381\ eV}{-14.63489\ eV}(0.91771) = 0.74081\ \ (15.112)$$

The valence energy of the carbon 2p is $-11.2603 \, eV$ and that of the Br AO is $-11.81381 \, eV$. The energy difference is less than that of $E_T \left(C - C, 2sp^3 \right)$ given by Eq. (14.151) for a single bond. Thus, $E_T \left(atom - atom, msp^3.AO \right)$ of the alkyl C - Br-bond MO in Eq. (15.52) due to the charge donation from the C and Br atoms to the MO is $-0.92918 \, eV$ (Eq. (14.513) based on 5 the maximum single-bond-energy contribution of the $C2sp^3$ HO. $E_T \left(atom - atom, msp^3.AO \right)$ of the series $CBr_m H_{4-m} \ m = 1,2,3$ is equivalent to those of methyl groups, $-0.72457 \, eV$ (Eq. (14.151)). For CBr_4 , $E_T \left(atom - atom, msp^3.AO \right)$ of the C-Br-bond MO in Eq. (15.52) due to the charge donation from the C and Br atoms to the MO is $-0.36229 \, eV$ (Eqs. (15.18-15.20 and Eq. (15.29) with a linear combination of s=1, $E_T \left(atom - atom, msp^3.AO \right) = -0.72457 \, eV$ 10 and $E_T \left(atom - atom, msp^3.AO \right) = 0$) based on the maximum charge density on the $C2sp^3$ HO.

The symbols of the functional groups of branched-chain alkyl bromides are given in Table 15.39. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl bromides are given in Tables 15.40, 15.41, and 15.42, respectively. The total energy of each branched-chain alkyl bromide given in Table 15.43 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.42 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that was subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The C-C bonds to the CHBr group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CBr group (no H bonds to C) were each treated as a tert-butyl C-C. E_{mag} is subtracted for each t-butyl group. In the case of 2,3-dibromo-2-methylbutane, E_{mag} is positive since the terms due to the two bromine atoms cancel that of the t-butyl and CH groups. The bond angle parameters of branched-chain alkyl bromides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.112) are given in Table 15.44.

Table 15.39. The symbols of functional groups of branched-chain alkyl bromides.

Functional Group	Group Symbol
CBr of CBr_mH_{4-m}	C-Br (i)
CBr of CBr_4	C-Br (ii)
CBr of $C_n H_{2n+2-m} Br_m$	C-Br (iii)
CH₃ group	$C-H$ $\left(CH_{3}\right)$
CH ₂ group	$C-H$ $\left(CH_{2}\right)$
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Parameter $C-Br(i)$ $C-Br(ii)$ $C-Br(iii)$ $C-H(CH)$ $C-H$	C-Br (i)	C-Br (ii)	C-Br (iii)	(- H (CH)	(C-H(CH))	H-3	C-C (a)	C-C (b)	C-C (6)	(g) ンーン	(e) ン-ン	C-C (#)
	Group	Group	i	Group	Group	Group	Group	Group	Group	Group	Group	Group
a (a,)	2,49163	2.52509	2.47329	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2,10725
c' (a _a)	1.83395	1.84622	1.82719	1.04856	1.05553	1.05661	1.45744	1,45744	1.45164	1.45744	1.45164	1,45164
Bond Length 2c' (A)	1.94097	1.95396	1,93381	1,10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Evn Bond			1 93	1,107	1.107		1.532	1.532	1,532	1.532	1.532	1.532
Jeneth	1,933	1.935	(1.1.1-tribromocthane)	(C-H propane)	(C-H propane)	1,122	(propane)	(propane)	(propane)	(propane)	(propane)	(propane)
	(methyl bromide)	(carbon tetrabremide)	1.950	1.117	1.117	(isobutane)	1.531	[.53]	1.531	1.531	1.531	1531
٨			(1,2-di	(C-H butane)	(C-H butane)		(butane)	(butane)	(butane)	(butane)	(butane)	(butane)
h,c (a_n)	1.68667	1.72265	1.66689	1.27295	1.29569	1.29924	1.54616	1,54616	1.52750	1.54616	1.52750	1.52750
	0.73604	0.73115	0.73877	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

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Table 15.41. The MO to HO Intercept geometrical bond parameters of oranched-chain anyl promides. A, A, are H or anyl groups.	etrical bond	parameters or D	rancheo-chain ai	kyi oromides.	ו'ע'ע מוב ע	or anyl groups.		ET 13 ET (man - man, map . Ac) .	.(/)						
Bond	Atom	β _τ (eV)	E _T (eV)	E ₇ (eV)	<i>E</i> ₇ (eV)	Final Total Energy	(a_0)	final (a,)	Ercatowh (eV)	$E(C2sp^3)$ (eV)	. _в	β, (°)	θ ³	$a_{\rm r}$	$\begin{pmatrix} d_{\dot{z}} \\ (a_o) \end{pmatrix}$
		Bond 1	Bond 2	Bond 3	Bond 4	(eV)			L III GI	Final					
$H_{\lambda-m}(', -Br_m, m=1,2,3, (C_n - Br (i))$	ڻ	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	68.10	067111	29.52	2,16808	0.33413
$H_{\lambda-m}C_{\alpha} - Br_{m}$, $m = 1,2,3$, $(C_{\alpha} - Br$ (i))	Br	-0,36229	8	0	0		1.15169	0.89582	-13.18804		68.10	111.90	29.52	2.16808	0.33413
$(C_a^B H_T)$ $(C_a - Br (ii))$	ڻ	-0.18114	Ø	0	0	-151,79683	17716.0	0.90664	-15,00689	-14 81603	66.10	113.90	28.76	2,21357	0,36734
(C_n, B_2) $(C_n - Br (ii))$	Br.	-0.18114	0	0	0		1.15169	0.90664	-15.00689		66.10	113.90	28.76	221357	0.36734
$-H_2(\zeta_n'Br)$ $(C_n-Br \text{ (iii)})$, C,	-0,46459	-0.92918	0	_ 0	-153.00946	0,91771	0.83885	-16.21952	-16.02866	62.67	117,33	26.55	2,21237	0,38518
$-H_{\underline{\mathcal{L}}',\overline{\mathcal{K}}',Br}$ (C _a – Br (iii))	Br	-0,46459	0	0	0	-	1.15169	0.88983	-15.29034		69.19	110.81	29.93	2.14337	0.31618
C - H (CH ₃)	i.	-0.92918	0	c	0	-152,54487	17716.0	0.86359	-15.75493	-15,56407	77.49	102.51	41,48	1,23564	0.18708
(- H ((H ₂)	i	-0.92918	-0,92918	0	0	-153.47406	17710.0	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0,29933
(-H (CH)	<u>.</u>	-0.92918	+0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17,61330	-17.42244	61.10	118.90	31.37	1,42988	0,37326
$H_{i}^{c}C_{i}C_{i}H_{i}CH_{3}-$	j, '	-0.92918	9	Đ	0	-152.54487	17716.0	0,86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_{\lambda}^{C}(\zeta, H_{\lambda}^{C}(H_{\lambda} - H_{\lambda}^{C}))$	ئ	-0.92918	-0.92918	С	0	-153.47406	17716.0	0,81549	-16.68412	-16,49325	56.41	123.59	26.06	1.90890	0.45117
$R - H_2C_c(H_2C_c - R)H(H_2 - (C - C \cdot b))$	ئن	-0.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2C_{\mu}(R - H_2C_{\mu})C_{\mu}(R^{\mu} - H_2C_{\mu})(H_2 - H_2C_{\mu})$	ئ	-0.92918	-0.72457	-0.72457	-0.72457	-154,71860	0,91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0,50570
$isoC_{i}C_{i}(H_{2}C_{i}-R^{i})HCH_{2}-$	ئن	-0.92918	-0.92918	8)676'0-	0	-154,40324	0,91771	0,77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$(wHC_{\alpha}(R'-H_{2}C_{\alpha})C_{\beta}(R''-H_{2}C_{\beta})CH_{\beta}-$	ئن	-0.72457	-0,72457	-0.72457	-0.72457	-154,51399	0.91771	0,76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$ler(C,C,\{H_2C,-R\}HCH_2-(C-C,f)\}$	້	-0.72457	-0.92918	-0.92918	0-	-154,19863	17710.0	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$(R' - H_2C_3)C_4(R' - H_2C_2)CH_2 - (R' - H_2C_2)CH_2 - (R' - H_2C_2)CH_2$	٠.,	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	0.91771	0.76763	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.42. The energy parameters (eV) of functional groups of branched-chain alkyl broinides.	(eV) of function	tal groups of branc	Hed-chain alkyr or	ominaes.			1700	1200	300	1500	(3) 0 - 0	(F)
Parameters	C-Br	. C-Br	C-Br	CH.	CH,	H-7	(a)	(a)	(c) (c)	(a)	(e)	נין ני קיטוני
	(E)	Group	(ii)	Group	Group	dnos	digin	dioio	diago	dinoio	dion	di di
"	1	-	-	3	2	-	-	-	1			1
	0	0	0	2	-	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0
	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
	0.74081	0.74081	0.74081	-	-	-	-	1		1	1	1
	_	_	-	1-	-	-	1	-	1	_	1	1
	-	-		17710	17716.0	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
7	0	0	0	0	-	1	0	0	0	1	1	0
ζ,	2	2	2	_	_		2	2	2	2	2	2
7 1	0	0	0		2	-	0	0	0	0	0	0
	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	6.5	0.5	0.5	0.5
	0.74081	0.74081	0.74081	_	_	-	-	-	I	1	1	-
V (eV)	-27.94806	-27.44996	-28.22940	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29,10112	-29.101.12
V (eV)	7.41885	7,36953	7,44631	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9,37273
7. (eV.)	5.60839	5.43544	5.70686	32.53914	21,06675	10.48582	6.77464	6.77464	00506'9	6.77464	6.90500	6,90500
V (eV)	-2.80419	-2.71772	-2.85343	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(w no) (eV)	-14.63489	-14.63489	14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15,56407	-15,35946	-15.56407	-15,35946	-15,35946
(Va) [in or,] (dV)	-0.72457	-0.36229	-0.92918	0	0	0	0	0	٥	0	0	0
E. (.10 110) (eV)	-13.91032	-14,27260	-13,70571	-15.56407	-15,56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
1; (u,sw) (eV)	-31,63533	-31.63531	-31.63537	-67.69451	-49,66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31,63535	-31.63535
E. (atom - atom, msp3.AO) (eV)	-0.72457	-0.36229	-0.92918	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1,44915	-1.44915
$E_{\tau}(xv)$ (eV)	-32,35994	-31,99766	-32,56455	-67,69450	-49.66493	-31.63537	-33.49373	-33,49373	-33.08452	-33.49373	-33,08452	-33.08452
a (1015 rad / s)	6.39733	6,27059	6.46864	24.9286	24,2751	24.1759	9,43699	9.43699	15.4846	9.43699	9,55643	9,55643
E. (eV)	4.21083	4,12741	4.25777	16.40846	15.97831	15.91299	6,21159	6.21159	10.19220	6.21159	6.29021	6.29021
E. (eV)	-0,13137	-0.12861	-0.13293	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Exam (aV)	0.07575	0.08332	0.07575	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0,12312 [2]	0.17978 [4]	0.09944	0.12312 [2]	0.12312 [2]	0.12312
E_ (eV)	-0.09349	-0.08695	-0.09506	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E (eV)	0.14803	0,14803.	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E. (thung) (eV)	-32,45343	-32.08460	-32.65961	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E L. no m) (eV)	14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
E	0	0	0	-13.59844	-13,59844	-13,59844	0	0	0	0	0	0
E. times (eV)	3.18365	2.81482	3.38983	12.49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.43. The total bond energies of branched-chain alkyl bromides calculated using the functional group composition and the energies of Table 15.42 compared to the experimental values [2]. The magnetic energy E_{ss} that is subtracted from the weighted sum of the E_b[csss+) (eF') values based on composition is given by (15.58). Formula Name

11000	Composition to Street by (13,30).												i				Same (a) Manual Control on the control of the cont	3
Formula	Name	C-Br (i)	C-Br (i) C-Br (ii) C-Br	C-Br (iii)	77.5	1117	0 7.7	0.11	.,,,,									
		:			, n	;;	(1)	(II) #3	(a)	(e) (-C)	(0)	C-C (d)	$C = C (a) \qquad C = C (b) \qquad C = C (c) \qquad C = C (d)$	C-C (f)	E		Experiment	Relative
																	ਲ	Епог
ė	F															Fremy (eV)	Total Bond	
1	1 en abromomethane	0	4	0	0	0	c	-			ļ						Energy (eV)	
CHBr	Tribromomethane	m	0	0	0	¢				> 0	۰ د	.	0	0	7		11.196	-0.00566
CHiBr	Bromomethane		0	0	, ,		- c		> 0	٥ د	.	0	0	0	0	12.87698	12,919	0.00323
CHB	Bromoethane	0	0	-		. –			> -		0 0	۰,	0	0	0		15.732	0.00360
C,H,Br	f-Bromopropane	0	0	_	-	. ~		o c				0	0	0	0		27.953	-0.00308
CH7Br	2-Bromopropane	0	0		7	0	. –		۱ د	.	> 0	۰,	φ.	0	0		40.160	-0.00093
CA logar	2,3-Dibromo-2-methylbutane	_	0	0	٣	0		· c		7 -	۰ د	0 6	φ,	0	0		40.288	-0.00024
C.H.J.Br	i-Bromohexane	0	0		_	v	٠ .		> v		7 0	o :	0	7	0		63.477	-0.00007
C,H,sBr	I-Bromoheptane	0	0	_	_	ص د			י נ	> <	0 0	0 (0	0	0		76.634	-0.00047
(,H;)	I-Bromooctane	0	0	_	_	7	. 0	· c	2 10	> 0	-	٥ ،	0 (0	0		88,783	0.00051
CIPHISH	l-Bromododecane	0	0	_	_	=	. 0		• =			٠,	0	0	0		100.952	-0.00033
Cirring	I-Bromohexadecane	٥	0	_		15		· c	: :			٥ (0 1	0	0		149.573	-0.00029
										,			٥	0	0		198.192	-0.00028

 E_T is $E_T(atom-atom,msp^2,AO)$ Table 15.44. The bond angle parameters of branched-chain alkyl bromides and experimental values [1]. In the calculation of heta, the parameters from the preceding angle were used.
 2C'
 2C'
 2C'
 Experiment
 Atom 1
 Experiment
 Atom 2
 Experiment
 Experiment

Exp. <i>θ</i> (°)	(methyl bromida) 113.2 (dibromomethane) 111.7	(hromoform)	(ultromomethans)	110 (1,2-dilumothane)	(1,1.1-trifarmoethane) 109.5	(1.1-dihromoethane)	(propare) (propare) (propare) (prutanc) (prutanc) (prutanc) (prutanc)	(Interest of 111.0 (Interest of 111.4 (Interest of	(isolutane)			110.8	(synames)	18.4	(150butane) [11.4	(isobutane)
<u>ه وي</u>	112.00	110,53	109.50	109.44	28 013	108,44	110.49	110.49	109.50	77 501	100 A4	19.67	110.76	111.27	111.27	07.50
(e) 10 m		ļ. <u>.</u>														
. (C		-				-			_	1			\perp	<u>.</u>		
e, ©	<u> </u>	-		70.36	-	-	69.51	15.60	_	70.56	70.56	_	+	-		72.50
(eV)	-0.9291R	0	c		-0.72457	0			C			-1.85836	0	0	-1.85836	
٧r 	0.89582	1.04887	1.15796		0.86359	1.15796			1.15796			0.81549	1.04887	1.04887	1.04887	
ช	_	67.0	0.75		-	0.75			0.75			-	0.75	0.75	0.75	
<i>;</i> '	0 74081 (Eq. (15.112))	0,86829 (Eq. (15 65))	_		0.74081 (Eu.(15.112))	-			-			-	-	_	-	
<i>-</i>	_	0.75	-		_	-			_			_	0.75	0.75	0.75	
C2 Mon 2	0.89582	0.91771	_		0.86359	-			_			0.81549	0.91771	0.9[77]	0 91771	
Aven 1	0.89582	0 87495	0.86359		0.86359	0.86359			0.86359			0.81549	0.87495	0.87495	0.87495	
Hybridization Designation (Table 15.3.A)	2	ž	=		뇬	=			=			25	-	-	_	
Confession 2	-15. [RNI4] Br	-11.813x1 Br	=		-11.81381 Br	=			=			-16,68412 (*	-14.82575 C,	-14.82575	-14.82575	
Tybridization Designation (Table 15.3.A)	ći .	•^	7		,	7			7			អ	w	10	۰,۰	
Alson I	-15.18604 Br	-15.55033	-(5.75493		-15,75493	-15,75493			-15.75493		1	-16,68412 C	-15.55033 (°,	-15.53033	-15 55033	
Tenneal Atens (a,)	6.0% [6	4.8312	3,4252		5,42,47	3,4252			3,4252	1	1	4.795R	4.1633	1 1633	- 4795x	
(a,)	3 66790	3 66790	2,09711		3,65437	211106	.,		1,09711	1	1	2.91547	2.11323	11760.5	2.91327	
(α _n)	3 66790	2.11106	2,09711		2 91547	2.11106			2.09711		+	2,91547	2,91547	2.91547	2.90327	
	ZBrC', Br (C', - Br (I))	ZHC_Br ((C Br (iii))	ZHC",H ZHC",H (C", - Br (iii))	$\angle C_sC_sH_s$ $(C_s - Br (iii))$		Methylene ZHC, H	7(, د, د, د	H, J, 72	1	7, 1, 17	H")" 77					7,7,7,7

ALKYL IODIDES
$$(C_n H_{2n+2-m} I_m, n=1,2,3,4,5...\infty m=1,2,3...\infty)$$

The branched-chain alkyl iodides, $C_nH_{2n+2-m}I_m$, may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein at least one H is replaced by an iodine atom. The C-I bond comprises a functional group for I replacing a H of methane (CH_3I) or for I replacing a H of an alkane corresponding to the series $C_nH_{2n+2-m}I_m$. The C-I bond of each of CH_2I_2 and CHI_3 comprise separate functional groups due to the limitation of the minimum energy of I matched to that of the $C2sp^3$ HO. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2CH)$ and t-butyl $((CH_3)_3C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the C-I functional groups comprises the hybridization of the 2s and 2p AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the I AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl iodides, the energy of iodine is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. Then, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of

To meet the equipotential condition of the union of the C-I H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.51) for the C-I-bond MO given by Eqs.

 $E(C,2sp^3) = -14.63489 \ eV$ (Eq. (15.25)). The I AO has an energy of $E(I) = -10.45126 \ eV$.

25 (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ I\right) = \frac{E(I)}{E(C,2sp^3)}c_2\left(C2sp^3HO\right) = \frac{-10.45126\ eV}{-14.63489\ eV}(0.91771) = 0.65537 \quad (15.113)$$

The valence energy of the carbon 2p is $-11.2603 \, eV$ and that of the I AO is $-10.45126 \, eV$. The energy difference is positive. Thus, based on the maximum charge density on the $C2sp^3$

HO $E_T(atom-atom,msp^3.AO)$ of the C-I-bond MO in Eq. (15.52) due to the charge donation from the C and I atoms to the MO is -0.36229~eV (Eqs. (15.18-15.20 and Eq. (15.29) with a linear combination of s=1, $E_T(atom-atom,msp^3.AO)=-0.72457~eV$ and $E_T(atom-atom,msp^3.AO)=0$) for methyl and alkyl iodides, -0.18114~eV for diiodomethane, 5 and 0 for CHI_3 .

The symbols of the functional groups of branched-chain alkyl iodides are given in Table 15.45. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl iodides are given in Tables 15.46, 15.47, and 15.48, respectively. The total energy of each branched-chain alkyl iodide given in Table 15.49 was calculated as the sum over the integer multiple of each $E_D(GPPPP)$ of Table 15.48 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that was subtracted from the weighted sum of the $E_D(GPPPP)$ (eV) values based on composition is given by Eq. (15.58). The C-C bonds to the CHI group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CI group (no H bonds to C) were each treated as a tert-butyl C-C. E_{mag} is subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl iodides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.113) are given in Table 15.50.

20 Table 15.45. The symbols of functional groups of branched-chain alkyl iodides.

Functional Group	Group Symbol
CI of CH_3I and $C_nH_{2n+2-m}I_m$	C-I (i)
CI of CH_2I_2	C-I (ii)
CI of CHI_3	C-I (iii)
CH₃ group	$C-H$ $\left(CH_{_{3}} ight)$
CH₂ group	$C-H$ $\left(CH_{2}\right)$
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

									[
	(B) 2-2	Group	2.10725	1.45164	1.53635	L.532 (propane) 1.531	(butane	1.52750	00009 0
	(e)))-)	Group	2.10725	1,45164	1.53635	1.532 (propane) 1.531	(butane)	1.52750	880090
	C-C (q)	Group	2.12499	1.45744	1.54280	1,532 (propane) 1,531	(butane)	1.54616	0.69600
	(e) 2-2	Group	2,10725	1.45164	1.53635	1,532 (propane) 1,531	(butane)	1.52750	888890
	(a) コーコ	Group	2.12499	1.45744	1,54280	1.532 (propane) 1.531	(butane)	1,54616	008800
	C-C (a)	Group	2.12499	1.45744	1.54280	1.532 (propane) 1.531	(butane)	1.54616	009890
	C-H	Group	1.67465	1.05661	1.11827	1.122 (isobutane)		1.29924	0.63005
values [1].	C-H(CH,)	Group	1.67122	1.05553	1,11713	1.107 (C-H propane) 1.117	(C-H butane)	1,29569	0 63150
des and experimental values [1]	C-H (CH.)	Group	1.64920	1.04856	1.10974	1.107 (C-H propane) 1.117	(C-H butane)	1,27295	0 62 500
hed-chain alkyl iodic	(iii) /2	Group	2,70662	2.03222	2,15081	2.15 (carbon tetraiodide)		1.78770	50032.0
Table 15.46. The geometrical bond parameters of branched-chain alkyl iodio	(ii) /3	Group	2,68865	2.02546	2.14365	2.132 (methył řodide)		1.76815	PEUSE O
The geometrical bone	(i) /-2	Group	2.67103	2.01881	2.13662	2.132 (methyl iodide)		1.74894	0.355.00
Table 15.46.	Parameter		a (a _p)	c' (a,)	Bond Length $2c'$ (A)	Exp. Bond Length	7	$b,c(a_n)$	

Вопа	Atom	E ₇ . (eV) Bond 1	/5, (eV) Bond 2	E _T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy C2sp³	$\binom{r_{outled}}{(a_0)}$	$\begin{pmatrix} f_{aa} \end{pmatrix}$	E _{Content} (eV) Final	$E(C2xp^3)$ (eV) Final	. _θ ©	, (O)	(6)	(a,)	$\begin{pmatrix} a_o \end{pmatrix}_{\tilde{\lambda}}$
(H.)	ن	-0,18[14	a	0	0	(eV)	17716.0	0,90664	-15.00689	-14,81603	69.63	110.37	29.08	2.33442	0,31560
(C, -1 (i))	7	-0.18114	0	0	0		1,30183	0.90664	-15.00689		69.63	110.37	29.08	2.33442	0.31560
-H ₂ C ₆ C ₁ -H ₂ C ₆ C ₁	نّ	-0.18114	-0.92918	0	0	-152,72602	17716.0	0.85377	-15.93608	-15.74521	63.16	116.84	25.82	2.40436	0.38554
- 1 (j) - 1 (j)	1	-0.18114	G	0	0		1.30183	0,90664	-15.00689		69.63	110.37	29.08	2.33442	0.31560
$C_{\mu}H_{2}I_{2}$	ئ	-0.09057	0	0	0	-151.70626	17710.0	0.91214	-14.91632	-14.72546	68.61	111.39	28.71	2,35818	0.33272
$C_aH_2I_2$	7	-0.09057	0	0	0		130183	0.91214	-14.91632		19.89	111.39	28.71	2.35818	0.33272
C_H, (iii)	ڻ	0	0	0	0	-151,61569	17716.0	0.91771	-14.82575	-14.63489	67.36	112.44	28.32	2.38256	0.35035
$C_{\mu}H_{\mu}$	1	C	c	0	0		1,30183	17716.0	-14.82575	-14,63489	67.56	112.44	28.32	2.38256	0.35035
('-H (CH')	Ü	-0.92918	0	0	0	-152,54487	17716.0	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1,23564	0,18708
C-H (CH.)	ú	-0.92918	-0.92918	0	0	-153,47406	17716.0	0.81549	-16,68412	-16.49325	68.47	111.53	35,84	1,35486	0.29933
C-H (CH)	i	-0.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.77247	-17,61330	-17.42244	61.10	118.90	31.37	1.42988	0,37326
H5C,C,H2CH2-	ڻ	-0.92918	0	C	0	-152.54487	17716.0	0.86359	-15,75493	-15,56407	63.82	116.18	30.08	1.83879	0.38106
H;C;C;H;CH2	ئ	-0.92918	-0.92918	a	0	-153,47406	17716.0	0.81549	-16.68412	-16.49325	56.41	123.59	26,06	1,90890	0.45117
$R - H_2C_{C_4}(H_2C_5 - R^4)HCH_2 - C_2C_4R_3$	ئن	-0.92918	-0.92918	-0.92918	0	-154.40324	122160	0,77247	-17,61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2^{-1}C_4(R' - H_2^{-1}C_3)C_4(R'' - H_2^{-1}C_3)CH_2 - CC_2^{-1}C_3$	ڻ	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0,75889	-17,92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(C-C, C_0)$	ئ	40.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1,97162	0.51388
(R' - R') = (R') = (R'	ئ.	-0.72457	-0.72457	-0.72457	-0,72457	-154,51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1,94462	0.49298
$(C - C \cap C)$ $(C - C \cap C)$	ئ	-0.72457	-0,92918	-0.92918	9	-154.19863	17710.0	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1,92443	0,47279
isaC. (R'-HzC.)C. (R'-HzC.)CHz-	ڻ	-0.72457	-0,72457	-0.72457	-0.72457	-154.51399	17716.0	0.76765	-17.92866	-17,73779	\$0.04	129.96	22.66	1.94462	0.49298

ible 15.47. The MO to HO intercept geometrical bond parameters of branched-chain alkyl iodides. R.R.R" are H or alkyl groups. E, is E, (atom - atom, nisp², AO).

Parameters	/-\ (e)	7-7	Parameters $C-I$ $C-I$ $C-I$ $C-I$ (ii) (iii) (iii) Green Green	CH ₃ Group	CH ₂ Group	C−H Group	C = C (a) Group	C~C (b) Group	C~C (c) Group	C-C (d) Group	C-C (e) Group	Group
ll.	-	-	_	m	2		-	1	1	1		-
n.	0	0	0	2	_	0	0	0	0	0	0	0
II.	0	0	0	0	0	0	0	0	0	0	0	0
	0.5	0.5	0.5	0.75	0.75	0.75	6.0	0.5	5'0	0.5	0,5	0.5
	0.65537	0.65537	0.65537	_	-	-	1	1	-	1	1	1
	-	-		-	_	-	1	_	_	1	1	I
	_	-	-	0.91771	0.91771	177160	17716.0	0.91771	0.91771	17716.0	0.91771	0.91771
7	_	0	_	0	-	1	0	0	0	1	1	0
	2	2	2	_	-	1	2	2	2	2	2	2
	0	0	0	m	2	-	0	0	0	0	0	0
	0.5	0.5	0,5	0.75	0.75	0.75	0.5	0.5	0.5	5'0	0.5	0.5
= -	0.65537	0.65537	0.65537			1	1	1	1	-	-	1
V (eV)	-26.59109	-26.34902	-26,10696	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29,10112	-28.79214	-29.10112	-29.10112
V (eV)	6.73951	6.71739	6.69505	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9,33352	9.37273	9.37273
T (aV)	4.97768	4.90005	4.82280	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V (eV)	-2.48884	-2.45002	-2.41140	-16.26957	-10,53337	-5.24291	-3,38732	-3,38732	-3.45250	-3,38732	-3.45250	-3.45250
Elso no (eV)	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15,56407	-15.35946	-15,35946
ΔE (10 110) (eV)	-0.36229	-0.18114	0	0	0	0	0	0	0	0	0	0
E_(10 10) (eV)	-14.29907	-14.45375	-14.63489	-15,56407	-15.56407	-14.63489	-15.56407	-15,56407	-15.35946	-15.56407	-15.35946	-15.35946
E. (u.m) (eV)	-31.63534	-31,63535	-31.63540	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31,63535	-31,63537	-31,63535	-31.63535
Er (atom - atom, msp2.AO) (eV)	-0.36229	-0.18114	0	0	0	0	-1.85836	-1.85836	-1,44915	-1.85836	-1.44915	-1.44915
E_(sto) (eV)	-31.99766	-31.81651	-31.63537	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33,49373	-33.08452	-33.08452
w (1015 rad/s)	10.2318	5.36799	9.90080	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9,55643	9.55643
E., (eV)	6.73472	3.53331	6.51688	16.40846	15,97831	15.91299	621129	6.21159	10.19220	6.21159	6.29021	6.29021
E. (eV)	-0.16428	-0.11832	-0.15977	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
E _{krio} (eV)	0.06608	0.06608	0.06608	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 (2)	0.17978 [4]	0.09944	0.12312 [2]	0,12312 [2]	0.12312 [2]
E (eV)	-0.13124	-0.08527	-0.12673	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E. (casp) (eV)	-32.12889	-31.90179	-31.76210	-67.92207	-49,80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E (c, 10:10) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489
Emmel (c, 40:110) (eV)	0	0	0	-13.59844	-13,59844	-13.59844	0	0	0	0	0	٥
E. (grum) (eV)	2,71108	2.63201	2.34429	12.49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

See on co.	C.C.) Vd dayin at dollared by	(80															,	,
Formula	Formula Name	.1	(ii) 1-2	C-1 (i) C-1 (ii) C-1 (iii) CH,	Œ,	CH,	() H)	CH (ii)	C-C (a)	CH (i) CH (ii) $C-C$ (a) $C-C$ (b) $C-C$ (c) $C-C$ (d) $C-C$ (e) $C-C$ (f)	(c) C-C	C-C (q)	C-C (e)	C-C (t)	(F)	Calculated Total Road	Experimental	Relative Error
																Energy (eV)	Energy (cV)	
				,	2	-	-	-	-	6	o	6	0	0	0	10.35888	10,405	0.00444
Ē	Linodomethane	> 0	> <	ne	2 0	÷	- =		, =	-	·c	-	0	0	7	12.94614	12,921	-0.00195
100	Dirodonychane	0	7	- :	٠.	-		2 5						-		15.20294	15.163	-0.00263
¥	fodomethane	_	0	•	_	.		> <	٠ -	> 0			: <		. <	27 36 DC4	27 343	-0 DOORS
H	fodoethane	_	=	0	_	_	0	>	-	>	>			> •	۰ د		1	20000
	Ted months	-	-	_	-	,	c	0	7	0	0	0	0	0	0	39,51834	39,516	-0.0000
127	1-todopropanc				٠.	, =	: -		ء ،	,	8	c	c	0	0	39,61923	39,623	0.0000
141	2-lodopropanc	-	=	0	7	•	-	2 1							-	51 0/057	51 800	0.0001
ž	2-Indo-2-methylpropane	_	ь	0	m	0	0	٥	0	-	-		2	,	-	21.20024	21.00	21000

[6													
	Exp. θ			111.2 (methyl iodido)			107 (propanc)	112 (propane) 113.8 (butane) 110.8 (isobutane)	111.0 (bulane) 111.4 (isobutane)				(isobutane)		111.4 (isobutane)	[11.4 (isobutane)	
	Cal. 6 (°)	112.10	112.39	109.50	109,44	111.86	108,44	110.49	110.49	109.50	109,44	109,44	110.67	110.76	111.27	111.27	107.50
	θ ₂ (°)																
	(°)			ĺ													
	θ (₀)				70.56			69.51	69.51		70,56	70.56					72.50
E_{τ} is $E_{\tau}(atom-atom,msp^3.AO)$	E_{T} (eV)	-0.3622R	0	0		-0.36228	0			0			-1.85836	0	0	-1.85836	
E_{r} is E_{r} (atom	<i>ي</i> ر	-	0.000001	1.15796		0.87495	1.15796			1.15796			0.81549	1.04887	1.04887	1.04887	
le were used.	5	1	0.75	0.75		-	0.75			0,75			_	0.75	0.75	0.75	
preceding ang	ర	0,65537 (Eq. (15,113))	0.76815 (Eq. (15.65))			0.65537 (Eq. (15.113))	1			_			1	1	1	-	
eters from the	ر.	-	0.75	_		-	-		-1	-				0.75	0.75	6.75	
f $\theta_{\rm v}$, the paran	C ₂ Atom 2		12216.0	-		0.87495	_			-			0.81549	0.91771	0.91771	17716,0	
e calculation o	C ₂ Atom I		12216'0	0,86359		0,87495	0,86359			0,86359			0.81549	0.87495	0.87495	0.87495	
experimental values [1]. In the calculation of $ heta_{\rm c}$, the parameters from the preceding angle were used.	Atom 2 Hybridization Designation (Table 15.3.A)	-	7	æ			ш			æ			3 2	-		-	
experimental	F cadomha Atom 2	-10.45126 I	-1045126 -1	Н		-10.45126 I	Ξ			±			-16.68412 (°,	-14.82575 C ₃	-14.82575 C,	-14.82575 C	
Ikyl iodides and	Atom I Hybridization Designation (Table 15.3.A)	-	-	7		ş	7			1			23	יי	ۍ	.S.	
ched-chain a	L'Crahenha Atom I	-10.45126 I	-14.82575	-15.75493		-15.55033	-15.75493			-15.75493			-16.68412 C,	-15,55033 C.	-15,55033	-15.55033	
rs of bran	$\frac{2c'}{\text{Tcewissal}}$ Atoms (a_n)	6.7205	5.2203	3.4252		5.7939	3.4252			3.4252			4,7958	4,1633	4.1633	4.7958	
paramete.	2c' thad 2 (a _n)	4 05092	4.03763	2.09711		4.03763	2.11106			2.09711			2,91547	2.11323	2.09711	2.90327	
bond angle	2c* Resid 1 (a ₀)	4.05092	2.11106	2.09711		2.91547	2,11106			2,09711			2.91547	2,91547	2.91547	2.90327	
Table 15.50. The bond angle parameters of branched-chain alkyl iodides and	Alesia of Angle	((C, -1 (ii))	(C, -1 (I))	ZHC, H ZHC, H (C, , - 1 (0))	ZC',C',H', (C', -1 (i))	(t) '-'',)) ''','''	Methylens ZHC, H	7٪.".	Н".Ј".)7	Methyl ZHC, H	7ر. در د	H".)"77	ייים נ" מנ"נ."נ.	"" C, F, H	L, C, H	امدر ر" 77.7°, ر"	"C,"C,"

ALKENYL HALIDES $(C_n H_{2n-m} X_m, n = 3,4,5... \infty m = 1,2,3... \infty)$

The branched-chain alkenyl halides, $C_n H_{2n+2-m} X_m$ with X = F, Cl, Br, I, may comprise alkyl and alkenyl functional groups wherein at least one H is replaced by a halogen atom. In the case that a halogen atom replaces an alkyl H, the C-X bond comprises the alkyl-halogen 5 functional groups given in their respective sections. The alkenyl halogen C-X bond comprises a separate functional group for each case of X bonding to the C=C-bond functional group given in the Alkenes section. In addition the CH group of the moiety XCH=C comprises a functional group unique to alkenyl halides. The straight and branched-chain alkenes, $C_n H_{2n}$, comprise at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. The three distinct functional groups given in the Alkenes section are C vinyl single bond to -C(C) = C, C vinyl single bond to -C(H) = C, and C vinyl single bond to $-C(C) = CH_2$. In addition, CH_2 of the $-C = CH_2$ moiety is also an alkene functional group solved in the 15 Alkenes section.

Consider the case where X=Cl substitutes for a carbon single bond or a hydrogen atom. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, two distinct C-Cl functional groups can be identified: Cl vinyl single bond to 20-C(C)=C and Cl vinyl single bond to -C(H)=C. The alkenyl-halide CH group is equivalent to that solved in the Hydrogen Carbide (CH) section except that $\Delta E_{H_2MO}(AO/HO)=-1.13379~eV$ in order to energy match to the C-Cl and C=C bonds.

The alkyl portion of the alkenyl halide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) 25 functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkene halides are equivalent to those in branched-chain alkanes.

 $E_T \left(atom-atom, msp^3.AO \right)$ of the C=C-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene, -2.26759~eV, given by Eq. (14.247). $E_T \left(atom-atom, msp^3.AO \right)$ of each C-C-bond MO in Eq. (15.52) is -1.85836~eV or -1.44915~eV based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, -0.92918~eV (Eq. (14.513), or methyl, -0.72457~eV (Eq. (14.151)), groups, respectively.

The solution of each C-X functional group comprises the hybridization of the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the X AO to form a MO permits each participating orbital to decrease in radius and energy. The alkenyl C-X-bond functional groups comprise single bonds and are equivalent to those of the corresponding alkyl halides except that the halogen AO and the C-X-bond MO are each energy matched to the alkene $C2sp^3$ HO. In alkenyl halides with X=Cl,Br, or I, the energy of the halogen atom is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. For example, the hybridization factor C_2 of Eq. (15.52) for the alkenyl C-Cl-bond MO given by Eq. (15.111) is $C_2(C2sp^3HO to Cl) = 0.81317$.

 $E_T(atom-atom,msp^3.AO)$ of the alkenyl C-Cl-bond MO in Eq. (15.52) due to the charge donation from the C and Cl atoms to the MO is -0.72457~eV for the Cl vinyl single 20 bond to -C(H)=C C-Cl group and -0.92918~eV for the Cl vinyl single bond to -C(C)=C C-Cl group. It is based on the energy match between the Cl atom and the $C2sp^3$ HO of an unsubstituted vinyl group and a substituted vinyl group given by Eqs. (14.151) and (14.513), respectively.

The symbols of the functional groups of branched-chain alkenyl chlorides are given in 25 Table 15.51. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkenyl chlorides are given in Tables 15.52, 15.53, and 15.54, respectively. The total energy of each branched-chain alkenyl chloride given in Table 15.55 was calculated as the sum over the integer multiple of each E_D (Group) of Table 15.54 corresponding to functional-group composition of the molecule.

The bond angle parameters of branched-chain alkenyl chlorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.111) are given in Table 15.56.

Table 15.51. The symbols of functional groups of branched-chain alkenyl chlorides.

Table 13.31. The symbols of functional group	ips of oranched-chain alkenyr emorides.
Functional Group	Group Symbol
Cl vinyl single bond to -C(H)=C	C-Cl (i)
Cl vinyl single bond to $-C(C)=C$	C-Cl (ii)
CC double bond	C = C
C vinyl single bond to $-C(C)=C$	C-C (i)
C vinyl single bond to -C(H)=C	C-C (ii)
C vinyl single bond to -C(C))=CH ₂	C-C (iii)
CH (alkenyl halide)	C-H (i)
CH₂ alkenyl group	$C-H\left(CH_{2}\right)$ (i)
CH₃ group	$C-H$ $\left(CH_{_{3}}\right)$
CH₂ alkyl group	$C-H\left(CH_{2}\right)$ (ii)
CH (alkyl)	C-H (ii)
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

									_
	(C-C)	Group		2.10725	1,45164	1.53635	1.532 (propane) 1.531 (butane)	1,52750	0.68888
	(e) ンーン	Group		2.10725	1.45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888
	C-C (q)	Group		2.12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	0.68600
	(e) U-U	Group		2,10725	1.45164	1,53635	1.532 (propane) 1.531 (butane)	1,52750	0,68888
	(a) 2-2	Group		2.12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	0.68600
	C-C (a)	Group		2.12499	1,45744	1.54280	1.532 (propane) 1.531 - (butane)	1.54616	0.68600
	C ~ H (ii)			1.67465	1,05661	1.11827	1.122 (isobutane)	1.29924	0.63095
	C-H(CH,)	Group	Group	1.67122	1.05553	1.11713	1.107 (C-H propane) 1.117 (C-H butane)	1.29569	0.63159
	$C \sim H(CH,)$	Group		1.64920	1.04856	1.10974	1.107 (C-H propane) 1.117 (C-H butane)	1,27295	0.63580
	() H-3	Group		1,60061	1.03299	1,09327	1.09 (vinyl chlorids)	1.22265	0.64537
	('H.) H -)	7	(i) Group	1.64010	1.04566	1.10668	1.10 (2- methylpropene) 1.108 (avg.) (1.3-hutadiene)	1.26354	0.63756
ital values [1].	-C-(III) C-	Group		2,04740	1,43087	1.51437	1.508 (2- methylpropene)	1.46439	0.69887
es and experimen	(!) (-)	Group		2,04740	1,43087	1,51437	1.508 (2-futene)	1.46439	0.69887
alkenyi chiorid	()-(.)	Group		2.04740	1,43087	1.51437		1.46439	0.69887
r pranched-chair	Ω = Ω	Group		1.47228	1.26661	1.34052	1.342 (2- nxdhylpropene) 1.346 (2-butene) 1.349 (1.3-hutahlène)	0.75055	0.86030
ond parameters c	Parameter C-Cl (i) C-Cl (C=C (C-Cl (i) C-C (ii)	(E)	Group	2,19358	1.64243	1.73827	1.730 (vnyl chloride) 1.73 (f.1)- dichlorochylene	1.45403	0 74874
he geometrical b.	(0)-0	Group		2.15818	1.62912	1.72419	1.730 (vinyt chloride) 1.73 (1,1- dichfurochylene	1.41552	0.75486
Table 15.52. 11	Parameter			a (a,)	c' (a,)	Bond Length 2c' (A)	Exp. Bond Length (A)	b,c (a,)	
	_	_			_				

Bond .	Atom	<i>ド</i> 子 (eV) Bond I	ائم (eV) Bond 2	7. ₇ (cV) Bond 3	ائم (وV) Bond 4	Final Total Energy ('2xp'	remeted (a.)	$f_{fin,s}$ (a_0)	$E_{i,\ldots}[(C2\eta^3)]$ (eV) Final	$E\left(\left(2\lambda p^{3}\right) \right)$ (eV) Final	θ, (•)	(₀)	(e)	(a,)	(a,)
$C_s = C_s(CI) - H\left(CH\right)$ (i)	ن	1.34946	-0.72457		c	(eV)	0,91771	0.81549	-16.68412	-16.49325	76.99	103.01	40.53	1,21653	0.18354
$-C_b = C_a(H)CI$ (C, $-CI$ (i))	ű	-1.13379	-0.73457	0	С	-153,47406	17716,0	0.81549	-16.68412	-16,49325	7943	100.57	34.49	1.77872	0.14960
$-C_{t} = C_{s}(H)CT$ (('_s - ('t))	<i>C</i> ,	-0,72457	0	0	C)		1.05158	0.87495	-15,35033		85.36	1974	38.03	56669.1	0.07083
-(, = (',(')'(') ((', -(')'(i))	ر'	1.13379	-0,46459	-0.92918	0	-154 14326	17716.0	0.78405	-17.35332	-17.16245	71.27	107.83	30.88	1.88253	0.24010
-C _b =C' ₁ (C)C' (C' ₁ -C'(6))	נז	-0,46459	6	0	0		1.05158	0.88993	-15.29034		83.62	96.38	37.46	1.74125	0.09882
$C_{\nu}(H)C_{\mu} = C_{\mu}H_{\nu}C_{\mu}$	ີ ບໍ	-1.13380	-0.92918	0	0	-153 67867	17716.0	0 80561	-16.88873	-16.69786	127.61	52.39	58.24	0.77492	0.49168
$C_{\nu}(H)C_{\nu} = C_{\nu}H_{2}$	ره	-1.13380	0	0	U	-152.74949	0.91771	0.85252	-15.95955	-15.76868	129.84	50.16	60.70	0.72040	0.54620
$C_{c}(C_{s})C_{s} = C_{s}H_{s}C_{s}$	ڻ.	-1.13380	-0.72457	-0.72457	0	-154.19863	17716.0	0.78155	-17.40869	-17.21783	126.39	53.61	56.95	0.80289	0.46371
$R_i^{C_s}H_1 - C_s(C) = C$ (C'-('')	. ບ້	-1.13380	-0,72457	-0.72457	0	-154.19863	17716.0	0.78155	-17.40869	-17.21783	660.88	119.12	67.72	1.81127	0.38039
$R_{C,h}^{C,h}(C') = C'$ (C' - C; (0)) (C' - C; (0)) (C' - C; (0))	౮	-0.72457	-0.92918	0	û	-153,26945	0.91771	0.82562	-16.4795]	-16.28864	67 40	112.60	31.36	1.74821	031734
$R_{i}C_{b}H_{2} - C_{a}(H) = C$ $(C - C_{a}(ij))$	Ü,	-1.13380	81626.0-	С	0	-153.67866	0.91771	0.80561	-16.88873	-16.69786	64.57	115.43	29.79	1.77684	0.34596
$R_iC_iH_2 - C_i(H) = C_i(C_i - C_i(H))$	ן ני	-0.92918	-0.92918	0	0	-153.47405	17716.0	0.81549	-16.68411	-16.49325	65.99	1[4,0]	30.58	1.76270	0.33183
$C - H\left(CH_2\right)(i)$	C	-1.13380	u	0	Û	-152.74949	0.91771	0.85252	-15,95955	-15,76868	77.15	102.85	41.13	1.23531	0.18965
C – H (CH,)	Ü	-0.92918	D	е	0	-152.54487	17716.0	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1,23564	0.18708
$C-H\left(CH_{2}\right)$ (ii)	C	+0,92918	-0.92918	o	ŋ	-153.47406	17716.0	0.81549	-16.68412	-16.49325	68 47	111.53	35.84	1.35486	0.29933
C - H (CH) (ii)		-0.92918	8)626'0-	-0.92918	0	-154,40324	0.91771	0.77247	-17.61330	-17,42244	61.10	118.90	31.37	1.42988	0,37326
$H_iC_jC_bH_2CH_2 - (C_i-C_i)$	C,	-0.92918	o	c	e	-152.5487	17716.0	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	038106
H,C,C,H;CH; – (C, – C, (a))	ڻ	81656'o-	x1626'0-	0	e	-153 47406	17716.0	0,81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R - H_2(C_*(H_2C_* - R^*)HCH_2 - (C - C^*(b))$	ڻ	81620:D-	81626'0-	-0.92918	Ð	-154,40324	177160	0.77247	-17.61330	-17,42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2C_s(R^s - H_2C_s)C_h(R^n - H_2C_s)CH_1 - (C - C^s)$	ڻ'	-0.92918	-0.72457	-0,73457	72127.0-	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$hanC_iC_i(H_iC_e - R^i)HCH_1 - (C_i - C_i(d))$	ڻ	x1676'0-	x1026/0-	8167670*	0	-154,40324	17716.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$ler(C_{a}(R^{*}-H_{1}C_{a})C_{b}(R^{*}-H_{2}C_{c})CH_{2}-(C^{*}-C^{*})CH_{2})$	ڻ	-0.72457	75457.0-	-0.72457	-0.72457	-154,51399	17716.0	0.76765	-17.92866	977.71-	30.04	129.9%	22.66	1.94462	0.49298
terrC,C, $\left(H_2C_c-R\right)HCH_2-\left(C-C'(f)\right)$	C,	-0.72457	-4:9291R	41.92918	ė	-154,19863	0.91771	0.78155	-17.40869	-17.21783	52.78	27.72)	24.04	1.92443	0.47279
isot', (R'-H,C',)C', (R"-H,C',)C'H,-	-												Ī		

Farameters	5 €.	Parameters $C-CI$ $C-CI$ (ii) (ii)	C=C Group	('-(' () Group	C-C (ii) Group	('-(' (ii) Group	('H', (i) Group	Group	CH, Group	CH ₂ (ii) Group	C-H (ii) Group	('-(' (a) Group	C-C (b) Group	C-C (c) Group	C-C (d)	C'-C' (e) Group	Group
	dno.5	dino.	-	-	-	-	2	-	5	2	-	-	-	-	-	-	~
"		- •	1			-	-	c	2	-	0	0	0	0	0	0	0
n,		9		,	,	,			0	0	0	0	0	0	0	0	0
<i>II</i> ,	3	= :	5	, ,	, ,	, "	27.0	37.0	0.75	0.75	0.75	0.5	50	50	0.5	20	0.5
	0.5	CO.	Cn	3	3 -	3	2 -	-	-	-	-	-	-	-	-	-	-
	0.81317	0.81517	0.91//1	-	- -	-	-			. -	-		-	-	-	-	-
			-	-	-	-	-		-	-	-	- 1		12210	12210	124100	177100
r,	-	-	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0,91771	0.91771	0.91771	0.91771	0.91771	1//160	1//1670	1//1670	17170
<i>c</i> ,	-	0	0	_	0	-	-	-	0	-	-	0	0		-	-	
3	23	2	4	2	2	2	_	-	1	-	-	7	2	2	2	2	2
	0	0	0	0	0	0	2	-	3	2	1	0	0	0	٥	•	٥
	0,5	0.5	0.5	6.5	0.5	0.5	0.75	0.75	0.75	0.75	0.75	0,5	0.5	0.5	0.5	50	0.5
	0.81317	0.81317	17710	_	-	-	-	1	-	1	1	-	-	-	-	-	-
l. (ef.)	-32.87721	-32.14474	-102.08992	-30,19634	-30.19634	-30,19634	-72,03287	-37.10024	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29,10112	-28.79214	-29.10112	-29.10112
F. (eV.)	8,35160	8.28394	21.48386	9.50874	9.50874	9,50874	26.02344	13.17125	38.92728	25.78002	12.87680	9.33352	9.33352	9,37273	9,33352	9.37273	9.37273
7 (eV)	7.61688	7,32700	34.67062	7,37432	7,37432	7,37432	21.95990	11.58941	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
f. (eF)	-3.80844	-3.66350	-17,33531	-3 68716	-3.68716	-3.68716	-10.97995	-5.79470	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3,45250	-3,38732	-3.45250	-3.45250
E(.o m) (el')	-14,63489	-14.63489	0	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15,56407	-15,35946	-15.56407	-15.35946	-15.35946
DEn Molin no (eV)	-3.71674	-3.19677	0	0	0	0	0	-1.13379	0	0	0	0	0	0	0	0	0
E (40 m) (el')	-10.91815	-10.97139	0	-14,63489	-14.63489	-14.63489	-14,63489	-13.50110	-15,56407	-15,56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15,35946
E. lusui (eV)	-31,63531	-31.63541	-63.27075	-31.63534	-31.63534	-31.63534	-49.66437	-31,63539	-67.69451	49.66493	-31.63533	-31.63537	-31,63537	-31.63535	-31.63537	-31.63535	-31.63535
E. (atom - atom, msp 'AO) (eV)	-1,44915	-0.92918	-2.26759	-1,44915	-1.85836	-1.44915	0	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
E (sed Cel')	-33 08452	-32.56455	.65.53833	-33,08452	-33,49373	-33 08452	-49.66493	-31,63537	-67.69450	-49.66493	-31.63537	-33.49373	-33,49373	-33.08452	-33.49373	-33.08452	-33.08452
m (101, rad (s)	8.31434	8.11389	43.0680	9.97851	16.4962	9.97851	25.2077	26,4826	24.9286	24.2751	24.1759	9.43699	9.43699	15,4846	9,43699	9.55643	9.55643
E (ef)	5.47264	5.34070	28,34813	6.56803	10.85807	6.56803	16.59214	17.43132	16.40846	15.97831	15.91299	6,21159	6.21159	10.19220	6,21159	6.29021	6.29021
E, (el')	-0.15312	-0.14888	-0.34517	-0.16774	-0.21834	-0,16774	-0.25493	-0.26130	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Ex. (eV)	0.08059	0.08059	0.17897	0.15895	0.09931	0.09931	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13,458)	0.35532 Eq. (13,458)	0.35532 Eq. (13.458)	0.12312	0.17978 [4]	0.09944	0.12312	0.12312 [2]	0.12312
Ē (e ^V)	-0.11282	-0.10859	-0.25568	-0.08827	-0.16869	-0,11809	-0.07727	-0.08364	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_ (eV)	0.14803	0,14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
External (eV)	-33,19734	-32.67314	-66.04969	-33.17279	-33.66242	-33.20260	-49.81948	-31,71901	-67,92207	-49.80996	-31.70737	-33,59732	-33,49373	-33.24376	-33.59732	-33.18712	-33.18712
E . le, 10 10) (cF')	-14,63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489
E le, 10 '10 (eV')	0	0	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	•	٥	0

Relative Error 0.00170 0.00071 (j) :)-:) <u>ي</u> ق . . . ပြု Table 15.55. The total bond energies of Danoched-chain all-kenyl chlorides calculated using the functional group composition and the energies of Table 15.54 compared to the experimental values [2L].

Fromtile Name C-CI C

Exp. θ		124 (vinyl chloride)	(vinyl chloride) 123.8 (1.1-dichlorochylene)	123.8 (1,1-dichlorochylene) 122.5 (vînyl chloride)			13.44 (1.3.54m; suitine: ChCcCe 12.17 (1.3.54m; suitine: CachCce CachCe CachCe CachCce CachCce CachCce		118.5 (2-mcliy(propene)	(2-m-ւկչկյութթու	107 (proyane)	112 (propane) 113.8 (butane) 110.8 (sobutane)	(butane) (futane) 111.4 (isobutane)				110.8 (isobutane)		111,4 (isobutane)	111.4 (isobutane)	
(°)	116.94	121.53	121.53	123.19	118.36	113.84	123.46	118.19	11631	121.85	108.44	110.49	110.49	109.50	109,44	109.44	110.67	110.76	111.27	12711	
().								123.46													
θ ['] ()		11694	116.94					118.36		16.31											
φ. ①												15.09	69.51		70.56	70,56					1
E, (eV)	0			-0.92918	o .	-1.85836.	-1.85836		e		0			0			-1.85836	O	0	-1.85836	
ۍ`	1.09775			0.86359	1.07647	0.81549	2,0180		1.17300		1.15796			96151.1			0.81549	1.04887	1.04887	1,04887	
c,	0.75			-	0.75	_	-		0.75		0.75			0.75			-	0.75	0.75	0.75	
	0.95310 (Eq. (15.65))			0.81317 (Eq. (15.111))	1		_		-		-		-	-			-	-	_	-	1
٠	0.75			-	0.75	_	-		-			,		-				0.75	6.75	0.75	
. Morm 2	0.91771		,	0,86359	0,91771	0,81549	0.81549		-		-		,	-			0,81549	0.91771	17716.0	0.91771	
. Monn ?	0.83600			0.86359	0 85252	0.81549	0,80561		0,x5252		0.86359			0.86359			0,81549	0.87495	0.87495	0.87495	
Atom 2 Hybridizaton Designation (Table 15.3A)	CI			כו	1	ਨ	ಸ		Н		=			Ξ			22	-	-	_	
Eradonta Man 2	-12.96764 (*)			-12,95764 CJ	-14.82575 (°,	-16.68411 C,	-16 68411 C.		=		Ξ			н			-16.68412 C.	-14.82575 C.	-14.82575 C,	-14.82575 C.	
Atum I Iyebidization Designation (Table 15.3.A)	2				2	.a			6		7			7			\$8	ın	·20	5	
Freehouse Month	-16,27490 (_,			-15.75493	-15,95954	-16.68411	-16,99873		-15.95955		-13,75493			-15,75493			-16.08412 (°,	-15,55033	-15,53033	-15.53833 C _k	١
2c' Terminal Moms (a,)	4.58119			5 1000	4 2895	4 7958	4.7539		3,4756		3,4252			3,4252			4.7958	4,1633	4.1633	4.7958	
2c' thomal2 (a,)	3,25/25			1 25825	2,46175	2.16(175	2.KG175		2.04578		2.11106			2 09711			2.91547	2.11323	11760.5	2.90327	
2c' Bond I (a,)	2,06598			25321	211333	2.K6175	1,5331		244578		2.11136			2.09711			2.91547	2.91547	2.91547	2.90327	
Atonix of Angle	(נ." –נג (נ))	$\angle C_{s} = C_{s}H$ $(C_{s} - CY(0))$	(C, -C' (i))	ZC' ₈ = C' ₂ C' (C' ₂ - C' ₃ (i))	$ZHC_{r,C_{r}}$ $(C_{r}(H)C_{r}=C_{r})$	(".)=".)(".) '2".". '2".".	(נ' = נ''נ') דנ"נ'נ'	ZHC. C.	$\angle HC_{\mu}H$ $(H,C_{\mu}=C_{\mu}C_{\mu})$	$AC_{i}C_{i}H$ $(H,C_{i}=C_{i}C_{i})$	Mehytene ZHC H	אנ"כ"נ	Н",5",37	Methyl ZHC H	7.5.7	H,7,72	کر _م ر رژ نه در	ZC,C,H in C,	ZC,C,H to C,	70,47,5 العاق	1 111

ALCOHOLS
$$(C_n H_{2n+2} O_m, n = 1, 2, 3, 4, 5...\infty)$$

The alkyl alcohols, $C_nH_{2n+2}O_m$, comprise an OH functional group and two types of C-O functional groups, one for methyl alcohol and the other for general alkyl alcohols. The alkyl portion of the alkyl alcohol may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alcohols are equivalent to those in branched-chain alkanes.

The *OH* functional group was solved in the Hydroxyl Radical (*OH*) section. Each C-O group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$. 15 shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl alcohols, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \ eV$ (Eq. (15.25)) and the O AO has an energy of $E(O) = -13.61806 \ eV$. To meet the equipotential condition of the union of the C-O H_2 -

20 type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the C-O-bond MO given by Eqs. (15.68) and (15.70) is

$$c_2\left(C2sp^3HO\ to\ O\right) = \frac{E(O)}{E(C,2sp^3)}c_2\left(C2sp^3HO\right) = \frac{-13.61806\ eV}{-14.63489\ eV}(0.91771) = 0.85395 \quad (15.114)$$

 $E_T(atom-atom,msp^3.AO)$ of the C-O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-1.65376 \, eV$ for the CH_3-OH C-O group. It is based on the energy match between the OH group and the $C2sp^3$ HO of a methyl group and is given by the linear combination of $-0.92918 \, eV$ (Eq. (14.513)) and $-0.72457 \, eV$ (Eq. (14.151)), respectively. For the alkyl C-O group, $E_T(atom-atom,msp^3.AO)$ is $-1.85836 \, eV$. It is based on the energy match between the O AO and the $C2sp^3$ HO of a methylene group where both energy contributions are given by Eq. (14.513).

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The symbols of the functional groups of branched-chain alkyl alcohols are given in Table 15.57. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl alcohols are given in Tables 15.58, 15.59, and 15.60, respectively. The total energy of each alkyl alcohol given in Table 15.61 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.60 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl alcohols determined using Eqs. (15.79-15.108) are given in Table 15.62.

י מיטים וישור symbols of functional groups of alkyl alcohols.	Group Symbol	НО	C-0 (i)	C-0 (ii)	$C-H\left(CH_{j}\right)$	$C-H$ (CH_1)	<i>H−J</i>	('-('(a)	C – C (b)	(3) (3)	C-C (d)	(; – (, (e)	(1-('th
LAUIC 12,21. THE SYMBOIS OF E	Functional Group	OH group	CH;OH C-O	Alkyl C-O	CH; group	CH ₂ group	ж.	CC bond (n-C)	CC bond (iso-C)	CC bond (tert-C)	CC (iso to iso-C)	CC (t to t-C)	CC (t to iso-C)

	T	Π		T			1	T
Group	2.10725	1.45164	1.53635	1.532	(propane)	1.531 (butane)	1.52750	0.68888
C-C (e) Group	2.10725	1.45164	1.53635	1.532	(propane)	1.531 (butane)	1.52750	0.68888
C-C (d) Group	2.12499	1.45744	1.54280	1.532	(propane)	1.531 (butane)	1.54616	0.68600
C – C (c) Group	2.10725	1.45164	1.53635	1.532	(propane)	1.531 (butane)	1.52750	0.68888
C - C (b) Group	2.12499	1.45744	1.54280	1.532	(propane)	(butane)	1.54616	0.68600
C – C (a) Group	2.12499	1.45744	1.54280	1.532	(propane)	(butane)	1.54616	0.68600
C-H Group	1.67465	1.05661	1.11827		1.122	(Isobutane)	1.29924	0.63095
$C-H\left(CH_{1}\right)$ Group	1.67122	1.05553	1.11713	1.107	(C-H propane)	1,117 (C-H butane)	1.29569	0.63159
$C-H\left(CH_3\right)$ Group	1.64920	1.04856	1.10974	1.107	(C-H propane)	(C-H butane)	1.27295	0.63580
C ~ O (ii) Group	1.78255	1.33512	1.41303		(.431	(etnanoi)	1.18107	0.74900
C-O (i) Group	1.79473	1.33968	1,41785		1.4246	(nethalio)	1.19429	0.74645
OH Group	1.26430	0.91808	0.971651	0.971	(ethanol)	(methanol)	0.86925	0.72615
Parameter	u (u ₀)	$c'(u_0)$	Bond Length $2c'(A)$	Exp. Bond	Length	(4)	$b,c(a_0)$	e

and the second of the second o		to discussion of a	inglement.		in the man is or any; groups, by to by and anomy any	LT to LT CHILL	. dem, more .								
Bond	Atom	ET	\vec{E}_T	E	Ē	Final Total	Luna	Final	Econtour	$E(C2sp^3)$,θ	θ	θ	d,	d,
		(eV) Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	$C2sp^3$ (eV)	(a ₀)	(a°)	(eV) Final	(eV) Final	©	(.)	·©	(a,)	(a°)
H,CO-H	0	-0.82688	0	0	0		1.00000	0.86923	-15.65263		115.49	64.51	64.51	0 54405	0 37403
$-H_2C_aO-H$	0	-0.92918	0	0	0		1.00000	0.86359	-15.75493		115.09	: 6491	10.00	0.55182	0.36635
$H_3C - OH$ (C - O (i))		-0.82688	0	0	0	-152.44257	17716.0	0.86923	-15.65263	-15.46177	96.59	83.4[46.30	1.23986	0.09981
$H_3C - OH$ (C - O (i))	0	-0.82688	0	0	0		1.00000	0.86923	-15.65263	-	96.59	83.41	46.30	1.23986	0.09981
$-H_2C_s - OH$ $(C - O \text{ (ii)})$	^ئ ت	-0.92918	-0.92918	0	0	-153,47405	0.91771	0.81549	-16.68411	-16,49325	93.09	86.91	43.59	1.29114	0.04398
$-H_2C_s - OH$ $(C - O(ii))$	0	-0.92918	0	0	0		00000 1	0.86359	-15.75493		97.20	82.80	46.50	1.22692	0.10820
$C - H\left(CH_3\right)$	Ü	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102,51	41.48	1.23564	0.18708
C-H (CH ₂)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1,35486	0.29933
('-H (CH)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118,90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2$ ($C-C_a$ (a))	C,	-0.92918	0	0	0	-152.54487	17716.0	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_1C_{\omega}C_{\omega}H_2CH_2 - (C - C^{*}(3))$	Ç	-0.92918	-0.92918	0	0	-153.47406	17716.0	0.81549	-16,68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R - H_2 C_a C_b (H_2 C_c - R^c) H C H_2 - (C - C^c (b))$	(,	-0.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2 C_o(R^o - H_2 C_d) C_o(R^o - H_2 C_c) C H_2 - (C - C_1 C_0)$	ن	-0.92918	-0 72457	-0.72457	-0.72457	-154.71860	17716.0	0.75889	-17,92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$ixoC_{r}(C_{r}(H_{2}C_{r}-R^{\prime})HCH_{2}-(C-C_{r}(d))$	C,	-0.92918	-0.92918	-0.92918	0	-154.40324	17716.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_{a}(R'-H_{2}C_{a})C_{k}(R''-H_{2}C_{c})CH_{2}-(C-C'(e))$	ن '	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0,49298
$ler(C_{r}(H_{2}C_{r}(H_{2}C_{r}-R)HCH_{2}-(C-C_{r}(f)))$	ڻ	-0.72457	-0.92918	-0.92918	0.	-154.19863	0.91771	0.78155	-17.40869	-17,21783	52.78	127.22	24.04	1.92443	0.47279
$ixoC_{\sigma}(R'-H_2C_{\sigma})C_{\kappa}(R''-H_2C_{\sigma})CH_2 - (C-C^{\circ}(f))$	ぴ	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.59. The MO to HO intercept geometrical bond parameters of alkyl alcohols. R,R',R' are H or alkyl groups. E_T is $E_T(atom-atom,mky^3,AO)$.

Jable 13.50. The energy parameters (e.v.) of functioning groups of darkyt at	2 (5 v) 01 1011011011	COOL	C-O (ii)	n.	77.5	C-H	C-C (a)	(F) (J-C)	(S) C) -(S)	C-C (d)	(e))-)	(J-)
raiametets	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
n,	-	_	-	3	2	1	1	1	1	1	-	-
n,	0	0	0	2	-	0	0	0	0	0	0	0
n.	0	0	0	0	0	0	0	0	0	0	0	0
(;	0.75	5.0	0.5	0.75	0.75	0.75	0.5	5.0	0.5	0.5	0.5	0.5
(;	_	-	-	-	-	_	_	1	1	-	-	
	0.75	_	-	-	-	_	-	_	1	1	1	1
6,	_	0,85395	0.85395	17716.0	0.91771	0.91771	17716.0	0.91771	0.91771	0.91771	0.91771	0.91771
<i>c</i> ,		0	0	0	-	-	0	0	0	1	1	0
	_	2	2		_	-	2	2	2	2	2	2
, , , , , , , , , , , , , , , , , , ,		0	0	3	2	1	0	0	0	0	0	0
(;	0.75	0.5	0.5	0.75	0.75	0.75	0.5	5.0	5.0	0.5	0.5	0.5
(,	1	1	-	-	1	-	1	-	1	1	1	1
V (cV)	-40.92709	-33.47304	-33.78820	-107,32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	14.81988	10.15605	10.19068	38.92728	25.78002	12.87680	9,33352	9,33352	9.37273	9.33352	9.37273	9.37273
T (eV)	16.18567	9.32537	9,47749	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V (eV)	-8.09284	-4.66268	4.73874	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(.v. 110) (eV)	-13.6181	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
15 (w m) (eV)	0	-1.65376	-1,85836	0	0	0	0	0	0	0	0	0
E. (so no) (eV)	-13.6181	-12.98113	-12.77653	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-15.35946
E. (n. 10) (eV)	-31.63247	-31.63544	-31.63529	-67.69451	-49.66493	-31,63533	-31.63537	-31.63537	-31,63535	-31,63537	-31.63535	-31.63535
$E_{\tau}(atom - atom, msp^3.AO)$ (eV)	0	-1.65376	-1.85836	0	0	0	-1,85836	-1.85836	-1,44915	-1.85836	-1.44915	-1.44915
$E_r(\iota n)$ (eV)	-31,63537	-33.28912	-33.49373	-67.69450	-49.66493	-31.63537	-33,49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
a (1015 rad / s)	44.1776	22.3978	12,2831	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_{Γ} (eV)	29.07844	14.74264	8.08494	16.40846	15.97831	15.91299	621129	6,21159	10.19220	621159	6.29021	6.29021
E. (aV)	-0.33749	-0.25287	-0.18841	-0.25352	-0,25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{\mathrm{Kuh}}$ (eV)	0.46311	0.12808	0.13328	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312	0.17978	0.09944	0.12312 [2]	0.12312 [2]	0.12312
En (eV)	-0.10594	-0.18883	-0.12177	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Eme (eV)	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\tau}(imuy)$ (eV)	-31.74130	-33.47795	-33.61550	-67.92207	-49.80996	-31.70737	-33,59732	-33.49373	-33.24376	-33,59732	-33.18712	-33.18712
Emilia (c, 20 117) (eV)	-13.6181	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489
Enthy (c. 10 10) (eV)	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
En Goorf (eV)	4.41035	4.20817	4.34572	12,49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Formula	Formula Name $OH C = O(i) C =$	Kyr alcohols ca	C $-O$ (i)	he functional gro $C = O$ (ii)	oup composition	n and the energ	ries of Table	15.60 compared	d to the experim	ental values [3						
		Group	Group	Group	6,773	, III ₂	3	(a)	(a) ((a)	(c) (c)	(a)	(e) C-C	C-C(E)	Calculated	Experimental	Relative
			•	•	ē									Total Bond	Total Bond	Error
CHTO	Methanol	-	0	_	-	0	-							Energy (eV)	Energy (eV)	
C ₂ H ₆ O	Ethanol	-	0		(-		> <	> -	> •	٥ (0	0	0	21.11038	21.131	0.00097
C,H _R O	I-Propanol		0	_		- ر		(> <	0 (0	0	0	33.40563	33.428	990000
CHYO	2-Propanol	-	c		. (۱ د	> -	7 (o (0	0	0	0	45.56333	45.584	0.00046
C _H H _{I0} O	1-Butanol	_	. 0		1	۰۰ ۳	~ c	7 6	-		0	0	0	45.72088	45.766	0.00098
$C_4H_{10}O$	2-Butanol		0	-		- ۱	> -	o (٥ (۰ ۵	0	0	0	57.72103	57.736	0.00026
CHIO	2-Methyl-1-propananol	_	0	. –	10			n c	5 (o (0 -	0	0	57.87858	57.922	0.00074
C ₁ H _{II} O	2-Methyl-2-propananol	_	0	-	ım	- c	- c	> <	200	، د	0 '	0	0	57.79359	57.828	0,00060
$C_{5}H_{12}O$	1-Pentanol	_	0.	_	. –	4	0 0	> •	> <	n (o (0	0	58.15359	58.126	-0.00048
$C_5H_{12}O$	2-Pentanol	_	0	-		٠,	> -	4 ~	> <	٥ (0	0	0	69.87873	69.887	0.00011
$C_5H_{12}O$	3-Pentanol	-	0	· —	10	10		+ •	> 0	.	0	0	0	70.03628	70.057	0.00029
$C_5H_{12}O$	2-Methyl-I-butananol	-	0		1 (۷ ر		4 C	5 r	0 0	0 (0	0	70.03628	70.07	0.00087
C ₅ H ₁₂ O	3-Methyl-I-butananol	,	0	_	2	1 ~		۷ -	n r	-	٥ (0 (0	69.95129	69.957	0.00008
C5H12O	2-Methyl-2-butananol	_	0	_	1 (**		- c		n c		- '	0	0	69.95129	69.950	-0.00002
C;H ₁₂ O	3-Methyl-2-butananol	_	0		; (*)	- c	۰ ر	- c) r	w) (0	0	0	70.31129	70.246	-0.00092
C,H,10	I-Hexanol		0	_			۱ د	> v	ກໍດ	> (- 1	0	0	18096'69	70.083	0.00174
C,H1O	2-Hexanol	_	0	_	2		· ·	יי	> 0	> 0	→ '	0	0	82.03643	82.054	0.00021
C,H _I ,O	I-Heptanol	provid	0		. –	, \	٠	n 4	> 0	,	ɔ (0	0	82.19398	82.236	0.00052
CHEO	I-Octanol	_	0		-	۰,	o c	7 C		o (5	0	0	94.19413	94.214	0.00021
C,H,O	2-Ethyl-1-hexananol		0		. ~	. "	> -	~ •	۰ د	0 0	0 (0	0	106.35183	106.358	0.0000
C ₃ H ₂₅ O	1-Nonanol	_	0	-	۰ -	3 ∝	- c	+ 0	n <		0 (0	0	106.42439	106,459	0.00032
$C_{10}H_{22}O$	1-Decanol	_	0	-			o c	٥ د	> 0	0 0	.	0	0	118.50953	118,521	0.00010
C12H26O	I-Dodecanol	_	0			`=	o c	\ <u>-</u>	> <	-	0 0	0	0	130.66723	130,676	0.00007
CleHao	1-Hexadecanol	-	0			· <u>'</u>	o c		> <	-	0 0	0 (0	154.98263	154.984	0.00001
							-		>	0	٥	0	0	203.61343	203.603	-0.00005

,									_						
	Exp. θ	108.53 (methanol)	(ethanol)	107.8 (ethanol)	107 (propane)	112 (propane) 113.8 (butane) 110.8 (isobutane)	111.0 (butane) 111.4 (isobutane)				(10,8 (isobutane)		111.4 (isobutane)	111.4 (isobutane)	
	Cal. <i>θ</i> (°)	107,24	106.78	110.17	108.44	110.49	110.49	109.50	109.44	109.44	110.67	110.76	111.27	111.27	107.50
	(°)														
	ι _θ			ĺ											
	φ̂ (©)					69.51	15.69		70.56	70.56					72.50
	E_T (eV)	0	0	-1,65376	0			0			-1.85836	0	0	-1.85836	
msp .AU).	c_i^t	0.91771	17716.0	0.83472	1,15796			1.15796			0.81549	1,04887	1.04887	1.04887	
nom – arom,	5'	67.0	0.75	1	0.75	٠		0.75			-	0.75	0.75	0,75	
L, 15 L, (<i>C</i> ,	1	+	1	-		DHC.	1			-	-	-	1	
e were used.	د'	52'0	0.75	1	-			1			1	0.75	0.75	0.75	
preceding angle	C ₁ Alem 2	17710	0.91771	0.85395 (Eq (15.114))				1			0.81549	0.91771	171100	17716.0	
ters from the	C ₂ Atom 1	_		0.81549	0.86359			0.86359			0.81549	0.87495	0.87495	0.87495	
n ot <i>e</i> ,, the parame	Atom 2 Hybridization Designation (Table 15.3.A)	-	-	0	ж			æ			25	1	-	-	
the catculation	Econtombic Atom 2	-14,82575	-14.82575	-13 61806	Ξ			ж			-16.68412 C.	-14.82575 C.	-14.82575 C,	-14,82575 C.	
ntal values [1]. In	Atom 1 Hybridization Designation (Table 15.3.A)	_	-	25	7			7			25	vs	vs	v.	
nd experime	Economic Atom I	-14.82575	-14.82575	-16,68412	-15,75493			-15,75493			-16.68412 (',	.")	-15.55033 C,	-15,55033 C,	
yl alcohols a	2c' Terninal Moms (a ₀)	3,6697	3.6515	4,5826	3,4252			3,4252			4 7958	4 1633	4 1633	4 7958	
neters of alk	2c' 2c' Bond I (a _p)	1,83616	1.83616	2.67024	2.11106			2.097[]			2.91547	2.11323	2.09711	2.90327	
l angle paran	2c' Bond I (q,)	2.67935	2.67024	2.91547	2,11106			2,09711			2.91547	2.91547	2.91547	2.90327	
Table 15.62. The bond angle parameters of alkyl alcohols and experimental values [1], in the calculation of θ_{ν} , the parameters from the preceding angle were used. E_{τ} is E_{τ} (atom — atom, they $-AU$).	Atoms of Angle	(C, O+, OH)	(C, -0 (ii))	(C, O (ii))	Mathylane ZHC; H	K',C,F,C,	H*5.77	Methyl ZHC, H	7,7,7,77	H*5.77	, 181 , 181 , 181	H",)".)7	/(", H H ₀ "), ool	املا (<u>. "</u> "کر"کر"ز (75,5,75

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ETHERS $(C_n H_{2n+2} O_m, n = 2,3,4,5...\infty)$

The alkyl ethers, $C_nH_{2n+2}O_m$, comprise two types of C-O functional groups, one for methyl or t-butyl groups corresponding to the C and the other for general alkyl groups. The alkyl portion of the alkyl ether may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2CH)$ and t-butyl $((CH_3)_3C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in ethers are equivalent to those in branched-chain alkanes.

Each C-O group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO 15 and the O AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ethers, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) and an energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)) and the O AO has an energy of $E(O) = -13.61806 \, eV$. To meet the equipotential condition of the union of the C - O H_2 type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the 20 C-O-bond MO given by Eq. (15.113) is $c_2(C2sp^3HO\ to\ O) = 0.85395$. $E_T(atom-atom, msp^3.AO)$ of the C-O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is -1.44915~eV for the $CH_3 - O -$ and $\left(CH_3\right)_3 C - O -$ C-O groups. It is based on the energy match between the O AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively), and the $C2sp^3$ 25 HO of a methyl group as given by Eq. (14.151). For the alkyl C-O group, $E_T(atom-atom, msp^3.AO)$ is $-1.65376 \, eV$. It is based on the energy match between the O AO and the $C2sp^3$ HO of a methylene group and is given by the linear combination of $-0.72457 \ eV$ (Eq. (14.151)) and $-0.92918 \ eV$ (Eq. (14.513)), respectively.

The symbols of the functional groups of branched-chain alkyl ethers are given in Table 15.63. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl ethers are given in Tables 15.64, 15.65, and 15.66, respectively. The total energy of each alkyl ether given in Table 15.67 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.66 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl ethers determined using Eqs. (15.79-15.108) are given in Table 15.68.

f alkyl ethers.	Group Symbol	() ()-)		(E) O L	C-H(CH,)	(e)	$C-H(CH_c)$	(2)	C-H	(4) 5-5	(a) (a)	(a) (-)	ر- ال (١٠)		(a)	ن ان (ه)	(2) 0	ر کار
Entries of alkyl ethers.	r unctional Group	C-O $(CH_3 - O - \text{ and } (CH_3), C - O -)$	C-O (alkyl)		Crts group		Criz group	CH	ر السماري	(1-t) ning (1-c)	CC bond (iso-C)	C trong (test C)	כר מסוום (נכונ-ר)	CC (iso to iso-C)	CC (t to t-C)		CC of to iso-C	(2010:1)

	()	Group		2.10725	1 45164	+010+1	1 52625	000000		1.532 foronane)	1.531	(butane)		1.52750	
	(e) C-C (e)	Group	•	2.10725	1.45164		1.53635		2021	1.532 (propane)	1.531	(butane)		1.52750	3333
	(p) 2-2	Group		2.12499	1.45744		1.54280		1 527	(propane)	1.531	(butane)		1.54616	002020
	(a) 2~2	Group	2 1000	2.101.2	1.45164		1.53635		1 532	(propane)	1.531	(butane)	1 87750	00/701	0 68888
	(q) 2-2	Group	2 12400	(/1417	1.45744		1.54280		1.532	(propane)	(4.45.2)	(outane)	1 54616	010101	0.68600
,	C-C (a)	dnoro	2,12499		1.45/44		1.54280		1.532	(propane)	(hutane)	(ommin)	1.54616	0,000	0.68600
	C-H Grown	dnoin	1.67465	1.05503	1.00001		1.11827		,	1.122 (isohutane)	ĺ		1.29924	0.62005	0.0000
	ن	Group	1.67122	1 05553			1.11713	1 107	(C~H)	propane)	1.117	(c - n outane)	1.29569	0.63159	7,7,7,7
rimental values [1]	$C-H\left(CH_3\right)$	Cronp	1.64920	1.04856			1.10974	1.107	H-2)	propane)	(C-H) hutane)	Culture to Co.	1.27295	0.63580	
Table 15.64. The geometrical bond parameters of alkyl ethers and experii	C – O (ii) Group	1 70,477	1.79473	1.33968		1 41705	60/11:1		1.418	(ethyl methyl ether (avg.))		1 10420	1.17429	0.74645	
The geometrical bond para	Group	1.80717		1.34431		1.42276			1.416	(dimethyl ether)		1.20776	0 77.300	0.74360	
Table 15.64.	ו מומוובוב	a (a _a)		c (a_0)	Bond	Length	2c' (A)	Exp Bond	Length	(F)		$b,c(a_0)$	0		

Table 15.65. The MO to HO intercept geometrical bond parameters of alkyl ethers.	trical bond	parameters of al		K, K', K'' are H or alkyl groups. E_{τ} is E_{τ} (diom - diom, insp. Ac)	ikyi groups. 127	15 Er (anom - 1	anon, map. A.	1.							
Bond	Atom	E,	E	E	ET	Final Total	rmiol	find	Ecoulomb	$E(C2sp^3)$.0	9	θ,	d,	72
		· 5	(e)	(eV)	(e.	Energy	(")		(e _V)	\ \{\sigma}	(0)	<u> </u>	(0)	(a)	(a)
		Bond 1	Bond 2	Bond 3	Bond 4	(eV)	(°)	(°n)	Final	Final	2			•	
$C-H\left(\partial C_{s}H_{s}\right)$	ن	-0.72457	0	0	0	-152.34026	17716.0	0.87495	-15,55033	-15,35946	78.85	101.15	42.40	121777	0,16921
$H_{C_a} - O - C_a H_3$ $(CH_3)_s C_a - O - C_s H_3$ $(CH_3)_s C_a - O - C_s (CH_3)_s$	**)	-0.72457	0	0	0	-152,34026	0,91771	0.87495	-15.35033	-15.35946	95.98	84.02	46.10	1.25319	0.09112
$H_{C_a}(C_{a}, C_{a}, C_{a},$	0	-0.72457	-0.72457	5	0		1.90000	0.83600	-16,27490		92.66	87.34	43.74	1.30535	0.03876
$-H_2C_a-OC_a(CH_3)_3$ $-H_2C_a-OC_aH_3$ $CC_A(CH_3)_3$	υ	-0.82688	-0.92918	0	0	-153.37175	0.91771	0.82053	-16.58181	-16.39095	92.41	87.59	43,35	1.30512	0.03456
$-H_1C_a - OC_b(CH_3)_A$ $-H_2C_a - OC_bH_3$ $(C - OC_bH_3)_A$	0	-0.72457	-0.82688	G	0		1.00000	0,83078	-16.37720		93.33	86.67	43,98	1.29138	0.04829
$-H_1C_u - O - H_2C_u - O - O - O - O - O - O - O - O - O - $	0	-0.82688	-0.82688	0	0		1.00000	0.82562	-16.47951		92.87	87.13	43.66	1.29829	0.04138
(C - H (CH ₁)	١	-0.92918	0	0	0	-152.54487	17710.0	0.86359	-15.75493	-15,36407	77.49	102.51	41.48	1.23564	0.18708
('-H (CH ₂)	C	-0.92918	-0.92918	0	0	-153,47406	17716.0	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
(C-H (CH)	Ü	-0.92918	-0,92918	-0.92918	0	-154,40324	17710.0	0.77247	-17.61330	-17.42244	01.10	118.90	31.37	1.42988	0.37326
H,C,C,H,CH,	ڻ	-0,92918	0	0	0	-152.54487	17716.0	0.86359	-15,75493	-15,56407	63.82	116.18	30.08	1.83879	0.38106
$H_1^{C}C_1H_2^{C}$ $(C-C_1^{C})$	ť	-0.92918	-0,92918	0	0	-153.47406	17716,0	0.81549	-16.68412	-16,49325	56.41	123.59	26.06	1.90890	0,45117
$(R - H_2C_s^*C_s)(H_2C_s - R)HCH_2 - (C - C^*(b))$	ť	-0.92918	-0.92918	81626:0-	0	-154.40324	17716.0	0.77247	-17.61330	-17,42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2C_a(R - H_2C_a)C_b(R^{n} - H_2C_c)CH_2 - CC_c = CC_c = CC_c$	نٔ	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	151.79	21.74	1.95734	0.50570
$lko(C_{\alpha}(K_{1}(H_{2}C_{\alpha}-R))HCH_{2}-IC_{\alpha}(H))$	ڻ	-0.92918	-0.92918	81626.0-	0	-154.40324	0.91771	0.77247	-17.61330	-17,42244	48,30	131.70	21,90	1.97162	0,51388
$uric_{a}(R^{*}-H_{2}C_{a})C_{a}(R^{*}-H_{2}C_{a})CH_{2} (C^{*}-C^{*}(e))$	ڻ	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	17719.0	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$ler(C,C,A,C,-R)HCH_2-(C,C,C)$	۲,	-0.72457	-0.92918	-0.92918	7	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24,04	1,92443	0,47279
$ixoC_{*}(R^{-}H_{2}C_{4})C_{*}(R^{-}H_{2}C_{s})CH_{2} (C^{-}C^{*}(f))$	ئن	-0,72457	-0.72457	-0.72457	-0.72457	-154.51399	12216 0	0,76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

ble 15.65. The MO to HO intercept geometrical band parameters of alkyl ethers. R,R,R' are H or alkyl groups. E_{τ} is $E_{\tau}(atom-atom,mxp^3AO)$.

Dominater: (1-0 (i) (-0 (ii)	C-0 (i)	(i) 0-0	Н.)	CH	H-,)	(e) .))	(a) 1-)	(c) 	ー fill コーン	ار د ا	·
Carameters	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
"	_	-	c	2	1	_	_	-	1	_	-
			2	-	0	0	0	0	0	0	0
"			c	0	0	0	0	0	0	0	0
113	2 2	50	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
	3 -	-	-	-	-	-	-	1	_	1	
	-	-	_	_	-	-	-	-	-	1	-
1,1	0.85395	0.85395	177100	17716.0	0.91771	17716.0	17/16/0	0.91771	0.91771	0.91771	0.91771
	6	0	0	-	-	0	0	0	-	_	0
5	2	2	-	-	-	2	2	2	2	2	2
<i>T</i>	0	0	5	2	_	0	0	0	0	0	0
***	0.5	0.5	0.75	0.75	0.75	0.5	0.5	5.0	0.5	0.5	0.5
, In	-		-	_	-	-	_	-	1	1	-
V (eV)	-33.15757	-33,47304	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_ (eV)	10.12103	10.15605	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
7 (47)	9 17389	9.32537	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V (eV)	-4.58695	-4.66268	-16.26957	-10,53337	-5.24291	-3,38732	-3.38732	-3.45250	-3.38732	-3,45250	-3,45250
E(v 10) (eV)	-14.63489	-14,63489	-15.56407	-15.56407	-14.63489	-15,56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
ΔΕ _{μ, 100} (.10 110) (eV)	-1.44915	-1.65376	0	0	0	0	0	0	0	0	0
E. (40 110) (eV)	-13.18574	-12.98113	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
E (u va) (eV)	-31.63533	-31.63544	-67,69451	-49,66493	-31,63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E\left(a_{000}-a_{000},n_{N}\sigma^{3},AO\right)\left(aV\right)$	-1.44915	-1.65376	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
F (10) (eV)	-33.08452	-33.28912	-67.69450	-49,66493	-31.63537	-33.49373	-33,49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (101s rad / s)	12.0329	12,1583	24.9286	24.2751	24.1759	9,43699	9.43699	15,4846	9.43699	9.55643	9.55643
F. (aV)	7.92028	8,00277	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
F (eV)	-0.18420	-0.18631	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
\overline{E}_{Krt} (cV)	0.13663	0.16118	0.35532	0.35532	0.35532 (Eq. (13.458))	0.12312	0.17978	0.09944	0.12312 (2]	0.12312 [2]	0.12312 [2]
F (eV)	-0.11589	-0.10572	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
(le (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E. Grap (eV)	-33,20040	-33.39484	-67.92207	-49.80996	-31.70737	-33,59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E . (c. 40 110) (eV)	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489
E (c. 10 110) (eV)	0	0	-13.59844	-13.59844	-13,59844	0	0	0	0	0	0
En (strup) (eV)	3.93062	4.12506	12.49186	7.83016	3,32601	4.32754	4,29921	3.97398	4.17951	3.62128	3.91734

															_				_				_	_				
Relative Error	0.00174	-0.00086	0000	3075	9039	0085	0081	-0 00055 FE000 0	-0.00218 0.00218	0000		Exp. θ (e)	:	112 (dimethyl ether)		(ethyl methyl ether)	109.4 (cthyl methyl cther)	107	(buobauc)	112 (propanc) 115.8 115.8 (bottanc) 110.8 (isobutanc)	(butanc) (butanc) (111.4				[10.8 (isobutane)		111.4 (isobutane)	111.4
		0.0	0.0	5 6	9 6	9	0,0	9	9 6	2		Cal. 6	:	17.54		25.111	109.13	108.44		110.49	61011	109.50	109.44	109.44	110.67	110.76	111.27	111.27
Experimental Total Bond Energy (eV)	32.902	57.500	57.355	57.499	82.088	82.033	94.438	106.122	106.425	161-001		6.0	>_															
	1	924	480	267	425	276	135	5 2	628			0.0		ļ	-		-	-	1			L	 		-	_	<u> </u>	_
Calculated Total Bond Energy (eV)	32.84496	57,54924	57.35	27.43369	82.06642	82.10276	94.36135	106.18004	106.65628			0, ©	<u>-</u>		+		-	_	1	(9.51	69.51	_	70.36	70.56			-	_
C-C (f)	٥٥	0	0 0	> 0	0 0	0	0	0 0	000	1	<u>.</u>	E _T (eV)		-1.85836		-1.85836	-1.65376	0		į		۵			-1,85836	0	0	-1.85836
(e) ()-()	00	0	00	,	o 0	0	0	00	900		$E_T(anom - anom, msp. AO)$	۲۰		0,78155		0.77699	0,83472	1.15796				1.15796			0.81549	1,04887	1,04887	1.04887
(g)	00	0	00	> <		0	0	9 0		,	IS Er (mom	υ ⁻		_	-	_	_	0.75				6.75	-		-	67.0	0.75	0.75
©	00	0 (00			3	m (- 0	, vo e	L	4	ئن!		_	-		-	-	1			_	-	_	-	-	-	-
_											ingle wer	1,		_		_		-				-			-	0.75	0.75	0.75
(a)	00	0 0	o (40	· 	0	~	o 4	. O W		e preceding a	C ₂ Atom 2		0.78155		0,77699	0,85395 (Eq. (15.114))	-			į	1			0.81549	0.91771	0.91771	17716.0
(a)	0 -	~ 0	7 0	9 4	o	-	۰,	۰ ۵	.00	1	micreis nom n	C ₂ Atom 1		0.78155		0.77699	0.81549	0.86359				0.86359			0.81549	0.87495	0.87495	0.87495
Group Group $(H_1, (H_2, (H_3, H_3, H_3, H_3, H_3))))))))))))))))))))$	0	0 (> -	- 0	<i>(</i> 4	0	- <) ri	. 0 ~	unhune [] In the coloniation of a the second control of	טון טו טיי, וווכ אמו	Atom 2 Hybridization Designation	(Table 15.3.A)	25		4	0	Ŧ				π			n	-	-	-
C#3	0 -	~ ~	v c	ণ ধ	9		0 1	9 64	0-	Ato colonfori	וווכ בשורווושוו	Frederic		-17,40869		-17.51099	-13 61806	35	1			I			-16.68412 C.	-14.82575	-14.82575	-14,82575
CH3	r1 r1	чг	v 11	, r1	য	4	ν (4 4	o vo			Atom I Hybridization Designation	(Table 15,3.A)			f †	25	1				-			25	'n		יט
Group	o	r) -		- 11	2			9 69	0 -	nd evnerine	חווו בעליבו חווו	f. Continuelya Atom 1		-17,40869		-17,51099	-וַפּ פּאַלוּוֹז	-15,75493				-15,75493			-16.68412 C,	-15.55033	-15,55033	-15,55033
Group	r)	6) -		. 6	0	_	- 4	0	~ ~	llay others	ing i chicks	2c' Teminal Atmax (a_)		4.4721		4,4385	4.5607	3.4252				3,4252			4.7958	4.1633	4.1633	4.7958
									į) Jo saletti	וווווווווווווווווווווווווווווווווווווו	2c' Bond 2 (a,)		2,64862		2.67935	2.67935	2.11106		`		2,09711			2.91547	2.11323	2,09711	2.90327
	Dimethyl ether Ethyl methyl ether	ether sonsi athar	Isopropyl methyl ether	1 ether	Diisopropyl ether	sthyl ether	L-Butyl isopropyl ether Ributyl schoo	Di-sec-butyl ether	Di-t-butyl ether -Butyl isobutyl ether	nd anole nare	md a Gim au	2c' Bond ((a _n)		2.68862		2,68862	2.91547	2,11106				2,09711			2,91547	2.9(547	2,91547	2.90327
										89 8	20 10 10 10 10 10 10 10 10 10 10 10 10 10	Atolits of Aligic		((:, '-0 (!)) "20".27	7.00".77	((,'' - 0 (!!))	((." -0 (!!)) 7(.*("0	Methytene ZHC, H		לנ"נ"נ"	н'.5`.)7	Methy!	7۲.۲.۳	H, 2, 12	ייי (." ענ"נ"נ"	2C, C, H	") ox	לנונ"ני"
	O'H'O		O H	O'H'	CoHio	CHIO		CHE	C,Hr,O	Table				`	Ľ	હ હૈ 	ِنْ ' ك			7	7	٧	7	7	7	7	1	7

PRIMARY AMINES
$$(C_n H_{2n+2+m} N_m, n = 1, 2, 3, 4, 5...\infty)$$

The primary amines, $C_n H_{2n+2+m} N_m$, comprise an NH_2 functional group and a C-N functional group. The alkyl portion of the primary amine may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and 5 methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in primary amines are equivalent to those in branched-chain alkanes.

The primary amino (NH_2) functional group was solved using the procedure given in the Dihydrogen Nitride (NH_2) section. Using the results of Eqs. (13.245-13.368), the primary amino parameters in Eq. (15.52) are $n_1 = 2$, $C_1 = 0.75$, $C_2 = 0.93613$ (Eqs. (13.248-13.249)), 15 $C_{1o} = 1.5$, and $c_1 = 0.75$. In primary amines, the $C2sp^3$ HO of the $C - NH_2$ -bond MO has an energy of $E(C,2sp^3) = -15.35946$ eV (Eq. (15.18) with s = 1 and Eqs. (15.19-15.20)) and the N AO has an energy of E(N) = -14.53414 eV. To meet the equipotential condition of the union of the N - H H₂-type-ellipsoidal-MO with the $C2sp^3$ HO, the hybridization factor c_2 of Eq. (15.52) for the N - H-bond MO given by Eq. (15.68) is

20
$$c_2(H \text{ to } 1^\circ N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.35946 \text{ eV}} = 0.94627$$
 (15.115)

The C-N group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. In primary amines, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)), and the N AO has an energy of $E(N) = -14.53414 \, eV$. To meet the equipotential condition of the union of the

C-N H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the C-N-bond MO given by Eqs. (15.68) and (15.70) is

$$c_2\left(C2sp^3HO\ to\ N\right) = \frac{E(N)}{E(C,2sp^3)}c_2\left(C2sp^3HO\right) = \frac{-14.53414\ eV}{-14.63489\ eV}(0.91771) = 0.91140 \quad (15.116)$$

 $E_T(atom-atom, msp^3.AO)$ of the C-N-bond MO in Eq. (15.52) due to the charge donation 5 from the C and N atoms to the MO is -1.44915~eV. It is based on the energy match between the N of the NH_2 group and the $C2sp^3$. HO corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups, -0.72457~eV (Eq. (14.151)), where the N-H bonds are also energy matched to the C-N bond.

The symbols of the functional groups of branched-chain primary amines are given in Table 15.69. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of primary amines are given in Tables 15.70, 15.71, and 15.72, respectively. The total energy of each primary amine given in Table 15.73 was calculated as the sum over the integer multiple of each E_D (Group) of Table 15.72 corresponding to functional-group composition of the molecule. The bond angle parameters of primary amines determined using Eqs. (15.79-15.108) are given in Table 15.74.

Table 15.69. The symbols of functional groups of primary amines.

Table 15.0%. The symbols of	runctional groups of primary a
Functional Group	Group Symbol
NH ₂ group	NH_2
C-N	C-N
CH₃ group	$C-H$ $\left(CH_{_{3}}\right)$
CH ₂ group	$C-H\left(CH_{2}\right)$
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Parameter NH C-N C-H CH CH	HN	C−.N	(HJ) H-J	(HJ) H - J	C-H	(= ((a)	(a) U-U	(e) U-U	(g) U-U	(e) ()-()	(E)
_	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
a (a ₀)	1.28083	1.92682	1.64920	1,67122	1.67465	2.12499	2.12499	2,10725	2.12499	2.10725	2.10725
c' (a ₀)	0.95506	1,38810	1.04856	1.05553	1.05661	1.45744	1.45744	1,45164	1.45744	1,45164	1.45164
Bond Length 2c' (Å)	8010:1	1,46910	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond	010	1 431	1.107	`	1 173	1.532	1.532	1.532	1.532	1.532	1.532
Length (A)	(methylamine)	(methylamine)	(C-A propare)	(C-H propane) 1.117 (C-H butane)	(isobutane)	(butane)	(propare) 1.531 (butane)	(propane) 1.531 (butane)	(propane) 1.531 (butane)	(butane)	(propanc) 1.531 (butane)
b,c (a ₀)	0.85345	1.33634	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e e	0.74566	0.72041	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.71. The MO to HO intercept geometrical bond parameters of primary amines.	trical bond	i parameters of p		R,R',R" are H or alkyl groups.	or alkyl groups.	E_T is $E_T(atou)$	E_T is $E_T(atom-atom,msp^3.AO)$.	.40)·							
Bond	Atom	E_{τ} (eV) Bond I	E _T (eV) Bond 2	E _T (eV) Bond 3	E _r . (eV) Bond 4	Final Total Energy (7.2xp³) (e.V)	(a ₀)	$\binom{r_{oo}}{a_o}$	Ecoulous (eV) Final	$E(C2sp^3)$ (eV) Final	,θ (₀)	, (°)	(e)	$\begin{pmatrix} d_i \\ a_o \end{pmatrix}$	$\begin{pmatrix} d_1 \\ (a_0) \end{pmatrix}$
$H_{\lambda}CN(H)-H$	N	-0.72457	0	0	0		0.93084	0.87495	-15.55033		118.00	62.00	64.85	0.54432	0.41075
$-H_2C_aN(H)-H$	2	-0.72457	0	0	0		0.93084	0.87495	-15,55033		118.00	62.00	64.85	0.54432	0.41075
H ₃ C - NH ₂	ن	-0.72457	0	0	0	-15234026	17716.0	0 87495	-15.55033	-15,35946	85.28	94.72	40.73	1.46010	0.07200
H ₃ C - NH ₂	×	-0.72457	0	0	0		0.93084	0.87495	-15,55033		85.28	94.72	40.73	1.46010	0.07200
-H ₂ C _s -NH ₂	ڻ' 'ن	-0.72457	-0.92918	0	0	-153.26945	17716.0	0.82562	-16.47951	-16.28864	80.20	99.80	37.50	1.52858	0.14048
-H ₂ C _s -NH ₂	N	-0.72457	0	0	0		0.93084	0.87495	-15.55033		82.28	94.72	40.73	1.46010	0.07200
$C-H$ (CH_3)	ر	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H$ (CH_2)	J	-0.92918	-0.92918	0	0	-153,47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
(H (CH)	ئ	-0.92918	-0,92918	-0.92918	0	-154,40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ ($C=C^{-}$ (a))	Ů,	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30,08	1.83879	0.38106
$H_3C_nC_nH_2CH_2 - (C-C_nC_n)$	บ้	-0.92918	-0.92918	0	0	-153,47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26,06	1.90890	0.45117
$R = H_2C_*C_*(H_2C_* - R^*)HCH_2 - (C - C^*(b))$	υť	-0.92918	-0.92918	-0 92918	0	-154,40324	177160	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2 C_a (R^a - H_2 C_a) C_b (R^a - H_2 C_c) C H_2 - (C - C, C_0)$	٦,	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-[7.73779	48.21	131.79	21.74	1.95734	0.50570
$IsoC_aC_b(H_2C_c - R^c)HCH_2 - (C - C^c(d))$	ີ່ ບໍ່	-0.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$ter(C_a(R^n - H_2C_a)C_A(R^n - H_2C_a)C_H_2 - (C_a - C_b)C_b)$	ζ,	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0,91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$ler(C,C,H_2C,-R')HCH_2-$ $(C-C,(f))$	<i>C</i> ,	-0,72457	-0.92918	-0.92918	.0	-154,19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_{\sigma}(R^{-}H_{2}C_{\sigma})C_{s}(R^{\sigma}-H_{2}C_{\sigma})CH_{2}-(C^{-}C_{\sigma}(f))$	C,	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Parameters	NH ₂	Parameters NH_2 $C-N$ Group	C.H.,	Croun	Group	Group	Group	Group	Group -	Group	Group
"	2	_	3	2	_	-	-	_	-	-	-
W	0	0	2	-	0	0	0	0	0	0	0
n,	-	0	0	0	0	0	0	0	0	0	0 .
	0.75	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0,5	0.5	0.5
(:	0.93613	-	-	_		-	_	1	1	1	-
6,	0.75	-	-	-	-	-	1	1	1		-
	0.94627	0.91140	17716.0	0.91771	0.91771	0.91771	17716.0	17716.0	0.91771	0.91771	0.91771
6,	0	0	0	-	1	0	0	0	1	1	0
, c		2	_		-	3	2	2	2	2	2
	2	0	3	2	-	0	0	0	0	0	0
	1,5	0.5	0.75	0.75	0.75	0.5	0.5	5.0	0.5	0.5	0.5
	_	-	1	_	-		_	-	1	-	1
V, (eV)	-77.89897	-32.46339	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	28.49191	9.80175	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	30,40957	8,42409	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V (eV)	-15.20478	-4.21204	-16.26957	-10.53337	-5.24291	-3.38732	-3,38732	-3.45250	-3.38732	-3.45250	-3.45250
E(se no) (eV)	-14.53414	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-15.35946
AF Line (10 10) (eV)	0	-1,44915	0	0	0	0	0	0	0	0	0
E, (40 110) (eV)	-14.53414	-13.18574	-15.56407	-15,56407	-14.63489	-15.56407	-15,56407	-15.35946	-15.56407	-15.35946	-15.35946
E(1, 20 10) (cV)	-14.53414	0	0	0	0	0	0	0	0	0	0
$E_{\tau}[u_{\lambda}u_{0}](eV)$	48.73642	-31.63534	-67.69451	-49,66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T \left(atom - atom, msp^3, AO \right) (eV)$	0	-1,44915	0	0	0	-1.85836	-1,85836	-1.44915	-1.85836	-1.44915	-1.44915
E_r [seq) (eV)	-48.73660	-33,08452	-67.69450	-49,66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
@ (1015 rad / s)	64.2189	18.9231	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E. (eV)	42.27003	12,45552	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
\vec{E}_{n} (cV)	-0.40690	-0,23100	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overrightarrow{E}_{\mathrm{Kuh}}$ (eV)	0.40929	0.12944	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978	0,09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
\vec{E}_{ac} (eV)	-0.20226	-0.16628	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{min}(eV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(\epsilon_{map})$ (eV)	-49.14112	-33,25079	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33,59732	-33.18712	-33.18712
Empel (c. 10 10) (eV)	-14.53414	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	14.63489	-14.63489	-14.63489	-14.63489
E (c, 30 10) (cV)	-13.59844	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
C 1 C.D.	0,000							00000		20000	

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Formula	Name	ME	210	27.0		T.	C-C (a)	(P)	(S)	(a)	(e)	白して	Calculated	cypennicalia	MENT PARTIES
name of		NH1	֝֞֞֝֝֞֝֞֝֝֞֝֞֝֞֝֞֝֞֝֞֝֞֝֓֓֞֝	, ,	֚֭֭֭֭֭֭֓֞֝֟֝֟֝֟֝֟֓֓֓֟֓֓֓֓֟֟	3					:	;	Total Bond	Total Bond	
		Group	Croup										Energy (eV)	Energy (eV)	
	Marketenins	-	-	-			0	0	0	0	0		23,88297	23.857	-0.00110
<u>.</u>	Menylanne								c	c	0	0	36,04067	36.062	0,00060
2,2	Emylanine		_ •		- •	• •		. <			-	c	48 19817	48.243	0.00092
Z C	Propytamine				۰, ۱	• •	4 ~	• <					60.35607	60.415	0.00098
Z ;	Butylamine			(n ~	o -	-				. =	. =	60 45696	60.547	0.00148
CHIN CHIN	sec-Bulylamine			4 -	- <	- c	- c	4 0	» r-			. 0	60,78863	217	-0.00118
Z Z	t-Butylamine			n r	> ~	-	0		. 0	• •	. 0		60,42863	60.486	0.00094

φ. φ	<u> </u>		107.1 (methylamine	110.3 (methylamine	108.0 hylamine) 107	(propane) 112 (propane) 113.8 (butane) 110.8 (isobutane)	11.0 stane) 11.4	in the second		T	110.8 (isobutane)	ì	111.4 (isobutane)	111.4 (isobutane)	
<u> </u>			 						+	-	-				-
Cal.	<u> </u>		108.40	110.48	108.44	110.49	110,49	109.50	109.44	109.44	110.67	110.76	111.27	111.27	
	<u> </u>									_	ļ.,				
	©			ļ								<u> </u>			
θ,	<u>۰</u>			-		69.51	15.69		70.56	70.56					
ET	(eV)		0	0	0			0			-1.85836	0	0	-1.85836	
25			1.05679	0.97194	1.15796			1.15796			0.81549	1.04887	1.04887	1.04887	
0			0.75	0.75	0.75			0.75			-	0.75	0.75	0.75	
.5	,		1	-	-			ų			-	-	-	-	
υ ₋			_	0.75	_						-	0.75	0.75	27.0	
5.	Atom 2		-	0.88583							0.81549	0.91771	0,91771	0.91771	
5	Atom		0.94627 Eq. (15.115))	0.91140 (Eq. (15.116))	0.86359			0.86359			0.81549	0.87495	0.87495	0.87495	
Atom 2 Hybridization	Designation	(Table 15.3.A)	н	Z	#			Н			25	_	_	-	
Eroniombuc	7 mont		н	-15.35946	π			н			-16.68412 C,	-14.82575 C,	-14.82575 C,	-14.82575 C	
Atom 1 Hybridization	Designation	(Table 15.3.A)	z	۰.				7			25	s,	87	5	
E minarke	2 FT	Atom 1	-14.53414	-14.53414	-15.75493			-15.75493			-16.68412 C,	-15.55033 C.	-15.55033 C,	-15,55033 C,	
2c' Teminal	∧tотs (<i>a</i> _g)		3.0984	3.8816	3,4252			3.4252			4.7958	4.1633	4,1633	4.7958	
2c' Bond 2	(a,)		1.91013	2.77620	2.11106			2,09711			2.91547	2,11323	2.09711	2.90327	
2c' Bond f	(a ₀)		1.91013	1.91013	2.11106			2.09711			2.91547	2.91547	2.91547	2.90327	
Albinsk of Angle 2c' 2c' 2c' Findwark Hybridization Findwark Hybridization C 2c' C' C' C' C' C' C' C' C'			ZHNH	ZHINC,	Methylene ZHC,H	אנ"כ"ל	ZC,C,H Methyl	н".)Н7	ZC,C,C,	ZC,C,H	کر''ر' ادا د''	ZC,C,H 50 C,	ZC,C,H isn C,	ZC,C,C,	7,5,5,7

SECONDARY AMINES
$$(C_n H_{2n+2+m} N_m, n=2,3,4,5...\infty)$$

The secondary amines, $C_n H_{2n+2+m} N_m$, comprise an NH functional group and two types of C-N functional groups, one for the methyl group corresponding to the C of C-N and the other for general alkyl secondary amines. The alkyl portion of the secondary amine may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carboncarbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in secondary amines are equivalent to those in branched-chain alkanes.

The secondary amino (NH) functional group was solved using the procedure given in the Hydrogen Nitride (NH) section. Using the results of Eqs. (13.245-13.316), the secondary amino parameters in Eq. (15.52) are $n_1 = 1$, $C_1 = 0.75$, $C_2 = 0.93613$ (Eqs. (13.248-13.249)), $C_{1o} = 0.75$, and $c_1 = 0.75$. In secondary amines, the $C2sp^3$ HO of the C-NH-bond MO has an energy of $E(C,2sp^3) = -15.56407 \, eV$ (Eqs. (14.514-14.516)); Eq. (15.29) with s=1 and s=2, Eq. (15.31), and Eqs. (15.19-15.20)) and the N AO has an energy of $E(N) = -14.53414 \, eV$. To meet the equipotential condition of the union of the N-H H_2 -20 type-ellipsoidal-MO with the $C2sp^3$ HO, the hybridization factor c_2 of Eq. (15.52) for the N-H-bond MO given by Eq. (15.68) is

$$c_2(H \text{ to } 2^{\circ}N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.56407 \text{ eV}} = 0.93383$$
 (15.117)

The C-N group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. In secondary amines, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)), and the N AO has an energy of $E(N) = -14.53414 \, eV$. To meet the equipotential condition of the union of the

C-N H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the C-N-bond MO given by Eq. (15.116) is $c_2\left(C2sp^3HO\ to\ N\right)=0.91140$.

As given in the Continuous-Chain Alkanes $(C_nH_{2n+2}, n=3,4,5...\infty)$ section, each methylene group forms two single bonds, and the energy of each $C2sp^3$ HO of each CH_2 group 5 alone is given by that in ethylene, $-1.13379\ eV$ (Eq. (14.511)). In secondary amines, the N of the NH group also binds to two $C2sp^3$ HOs and the corresponding $E_T(atom-atom,msp^3.AO)$ of each C-N-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is $-1.13379\ eV$. It is based on the energy match between the N of the NH group to that are equivalent to those of independent methylene groups, $-1.13379\ eV$ (Eq. (14.511)), where the N-H bond is also energy matched to the C-N bonds. $E_T(atom-atom,msp^3.AO)$ of the C-N-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is $-1.13379\ eV$. It is based on the energy match between the N of the NH group to two $C2sp^3$ HOs corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups, $-0.72457\ eV$ (Eq. (14.151)), where the N-H bonds are also energy matched to the C-N bond.

The symbols of the functional groups of branched-chain secondary amines are given in Table 15.75. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of secondary amines are given in 20 Tables 15.76, 15.77, and 15.78, respectively. As in the case of NH_2 (Eq. (13.339)), $C_{1o} = 2C_1$ rather than $C_{1o} = C_1$ in Eq. (15.52) for the C - N bond. The total energy of each secondary amine given in Table 15.79 was calculated as the sum over the integer multiple of each E_D (Group) of Table 15.78 corresponding to functional-group composition of the molecule. The bond angle parameters of secondary amines determined using Eqs. (15.79-15.108) are given in Table 15.80.

Table 15.75. The symbols of functional groups of secondary amines.

Functional Group	Group Symbol
NH group	NH
C-N (methyl)	C-N (i)
C-N (alkyl)	C-N (ii)
CH₃ group	$C-H\left(CH_{3}\right)$
CH₂ group	$C-H$ $\left(CH_{2}\right)$
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

lable 15.76.	Table 15.70. The geometrical bond parameters of secondary anines and experimental values [1]	and parameters of seco	חותם ל מנוווים מווח י		-							
Parameter	Group	C-N (i) Group	C – N (ii) Group	$C - H\left(CH_3\right)$ Group	$C-H(CH_2)$ Group	C−H Group	C – C (a) Group	C-C (b) Group	C – C (e) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\sigma\left(a_{_{0}}\right)$	1.26224	1.94862	1.94862	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'(a_b)$	0.94811	1.39593	1,39593	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1 45164	145164
Bond Length 2c' (A)	1.00343	1.47739	1.47739	1.10974	1,11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (A)	1.00 (dimethylamine)	1.455 (dimethylamine)		1.107 (C - H propane) 1.117	1.107 (C~H propane) 1.117	1.122 (isobutane)	1.532 (propane) 1.531	1.532 (propane) 1.531	1.532 (propane) 1.531	1.532 (propane) 1.531	1.532 (propane) 1.531	1.532 (propane) 1.531
h,c (a_0)	0.83327	1.35960	1.35960	1.27295	1.29569	1.29924	(outane)	(butane)	(butane)	(butane)	(butane)	(butane)
υ	0.75113	0.71637	0.71637	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	01040.1	1.32/30	1.52750

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Length (d	1.00 (dimethylamine)	1.455 (dimethylamine)		<u></u>	(C - H propane)	(C ~ H propane)		1.122 (isohutane)	(propane)		(propane)	(propane)	(propane)		(propane)	(propane)	
+	_		_		(C-H butane)	(C-H bu		(2)	(butane)		(butane)	(butane)	(butane)		1.531 (hiitane)	1.531 (hutane)	
h,c (a ₀)	0.83327	1.35960	1.35960	09,	1.27295	1.29569	•	1.29924	1.54616		1.54616	1.52750	1,54616		1.52750	1.52750	Τ
e e	0.70113	0.71637	0.71637	37	0.63580	0.63159		0.63095	0.68600		0.68600	0.68888	0.68600		0.68888	0.68888	
Table 15.77. The	Table 15.77. The MO to HO intercept geometrical bond parameters of secondary amines.	ept geometrical	bond paramete	rs of second		ν', R" are H c	or alkyl group	R, R', R'' are H or alkyl groups. E_T is $E_T(alom - alom, msp^3.AO)$	tom ~ atom, ms	p³.40).							
Bond		Atom	_	L	-	11	Į.	Final Total			4	1					
						+ \{\sigma}	£ 5	Energy	mind	final	Contomb	$E(C2sp^3)$.0	θ.	θ_1	ď	ď
			Bond 1		Bond 2 Bc	Bond 3	(ev) Bond 4	C2xp3	(a ₀)	(%)	Final	(eV) Final	<u> </u>	<u> </u>	©	(a0)	(a_{o})
H.C NIC H 1-H	H		†	+	2000	1		(eV)									
-H.C. N(R.)-H	H	× 3	+	+	0.56690	0	0		0.93084	0.85252	-15.95954		118.18	61.82	64.40	0.54546	0.40264
1 2 A 11 1 1 1		× :	+	+	-0.56690	0	0		0.93084	0.85252	-15.95954.		118.18	61.82	64.40	0.54546	0.40264
$H \cap AH \cap AH$	H3	: "ن	\dashv	+	0	0	0	-152.18259	17716.0	0.88392	-15.39265	-15.20178	84.14	95.86	40.30	1.48625	0.09032
ייט וואי טת	E 23	2 (+	-	-0.56690	0	0		0.93084	0.85252	-15.95954		80.95	99.05	38.26	1.53008	0.13415
אין - איז - רייו	N4.		+	-	-0.92918	0	0	-153.11177	17716.0	0.83360	-16.32183	-16.13097	78.89	101.11	36,99	1.55650	0.16057
-H ₂ C _n - NH - C _b H ₂	·6H2-	N	+	+	-0.56690	0	0		0.93084	0.85252	-15.95954		80.95	99.05	38.26	1.53008	0.13415
$C = H (CH_3)$		١	-0.92918	81	0	0	0	-152.54487	17716.0	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1,23564	0.18708
$C-H$ (CH_2)			-0.92918		-0.92918	0	0	-153.47406	17716.0	0.81549	-16.68412	-16,49325	68.47	111.53	35.84	1.35486	0.29933
C-H (C.H.)		٢	-0.92918		-0.92918 -0.5	-0.92918	0	-154,40324	0.91771	0.77247	-17,61330	-17,42244	61.10	118.90	31.37	1.42988	0.37326
$H_1C''_1C_1H_2C'H_1 - (C - C''_1(a))$, C,	.0.92918	<u></u>	0	0	0	-152.54487	17716.0	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$ H_1C_sC_sH_2CH_2 - (C - C_s(a)) $		ີ -	-0.92918		-0.92918	0		-153.47406	17716.0	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	08061	0.45117
R-H.C. (H.C - R')HCH -	- R')HCH -		╀	+													11102-70
((, -(, (p))	, , ,	້	-0,92918		-0.92918 -0.9	-0.92918	0	-154,40324	17716.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0,51388
$R - H_2C_u(R^* - H_2C_d)C_h(R^{**} - H_2C_c)CH_2$ $(C - C_1(Q))$	C _d)C _h (R"—H ₂ C,	.)CH ₂ - C _k	-0.92918		-0.72457 -0.7	-0.72457	-0.72457	-154.71860	17716.0	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_k(H_2C_c - R^1)HCH_1 - (C - C_c(d))$?') HCH₁ −	ບ້	-0.92918		-0.92918 -0.9	-0.92918	0	-154.40324	17716.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$Ier(C_{\sigma}\{R-H_2C_{\sigma}\}C_{\kappa}\{R^{n-}-H_2C_{\sigma}\}CH_2-\{C-C^{*}(\mathbf{e})\}$	C,(R"-H2C,)C	42- C,	-0.72457		-0.72457 -0.7	-0.72457	-0.72457	-154,51399	17716.0	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$IwrC_{s}C_{s}(H_{2}C_{s}-R^{s})HCH_{2}-(C-C^{s}(f))$	R') HCH ₂ –	ť	-0.72457		-0.92918 -0.9	-0.92918	-0	-154,19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$[isoC_{,a}(R'-H_2C_{,a})C_{,b}(R''-H_2C_{,c})CH_2 - (C'-C,C))$	C,(R"-H2C,)CF	l ₂ - C _k	-0.72457		-0.72457 -0.7.	-0.72457	-0.72457	-154,51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
								1									

		Table 19.75. The circles parameters (5.7) or through the property of the circles	, and									400
Parameters	NH Group	C ~ N (1) Group	Group	CH,	CH ₂	C → H Group	Group	Group	Group	Group	Group	Group
n,	1	-	1	3	7	_	-	-		-	1	1
n,	0	0	0	2	-	0	0	0	0	0	0	0
n,	0	0	0	0	0	0	0	0	0	0	0	0
	0.75	. 0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0,5	0.5	0.5
C,	0.93613	-	-	-	-	_	1	-	1	-	1	1
¢,	0.75	-	_	-	1			1	1	1	1	1
, 5	0.93383	0.91140	0.91140	17710	17716.0	0.91771	17716.0	0,91771	0.91771	17716,0	0.91771	17716.0
	-	0	. 0	0		-	0	0	0	1	1	0
£,		2	2	1	1	-	2	2	2	2	2	2
ŭ	-	0	0	3	2		0	0	0	0	0	0
C.	0.75	-	-	0.75	0.75	0.75	0.5	0.5	5.0	0.5	6.0	0.5
(."	-	-	-	_	-	1	_	-	1	1	1	1
V, (eV)	-39.21967	-31.98456	-31.98456	-107.32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (aV)	14.35050	9.74677	9.74677	38.92728	25.78002	12.87680	9,33352	9.33352	9,37273	9.33352	9.37273	9.37273
T' (eV)	15.53581	8,20698	8.20698	32,53914	21.06675	10.48582	6.77464	6.77464	6,90500	6.77464	6.90500	6.90500
V. (eV)	-7.76790	4.10349	-4.10349	-16,26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(so no) (eV)	-14.53414	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15,56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
ΔΕ _{11,310} (.10 110) (eV)	0	-1.13379	-1.13379	0	0	0	0	0	0	0	0	0
Er (30 110) (eV)	-14,53414	-13,50110	-13.50110	-15,56407	-15.56407	-14.63489	-15,56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
$E_T(u_2 x \sigma)$ (eV)	-31,63541	-31.63540	-31.63540	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T \{atom - atom, msp^3, AO\} (eV)$	0	-1.13379	-1.13379	0	0	0	-1.85836	-1.85836	-1.44915	-1,85836	-1.44915	-1.44915
$E_r(xv)$ (eV)	-31.63537	-32.76916	-32.76916	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (1015 rad 1s)	47.0696	15.1983	26.0778	24.9286	24,2751	24.1759	9.43699	9,43699	15.4846	9.43699	9.55643	9.55643
E. (aV)	30,98202	10.00377	17.16484	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
\vec{E}_{D} (eV)	-0.34836	-0.20505	-0.26859	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
\vec{E}_{Knh} (eV)	0.40696	0.12944	0.11159	0,35532 (Eq. (13,458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944	0.12312 [2]	0.12312	0.12312 [2]
E. (eV)	-0.14488	-0.14033	-0.21280	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mg} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E, (imp) (eV)	-31,78025	-32,90949	-32.98196	-67.92207	-49.80996	-31.70737	-33,59732	-33.49373	-33,24376	-33,59732	-33.18712	-33.18712
Emma (c. 10 110) (eV)	-14,53414	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489
E minut (cs. 10 110) (eV)	-13.59844	0	0	-13,59844	-13.59844	-13.59844	0	0	0	0	0	0
E., (Grup) (eV)	3.50582	3.63971	3.71218	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

E.p. [c.ww] (et') 3.50582 3.63971 3.71218 12.49186 7.83016 3.32601 4.2354 4.29921 3.97398 4.17951 3.5712 2.5012 2.49186 3.2012 3.97398 4.17951 3.5712 3.57		1									-	_		
15.79. The total bond energies of secondary amines calculated using the functional la Name NH $C-N$ (i) $C-N$ (ii) $C-N$ (ii) Group Group Group Group Dimethylamine i 0 2 Dispropriamine i 0 2		1/659.	3.71218	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	-	3.91734	
15.79. The total bond energies of secondary amines calculated using the functional lia Name $NH = C - N (i) C - N (ii)$ and $C - N (ii) C - N (ii)$ Group Group Group Group Dimethylamine i 2 0 Dimethylamine i 0 2] 					5					
ide Name NH C - N (i) C - N (i) Dimetivlamine Group Group Group Dischylamine 1 2 0 Dispopulamine 1 0 2 Dispopulamine 1 0 2	energies of secondary amines of	calculated using	the functional g	TOUD COMPOSITIC	un and the energie	s of Table 15./8	compared to the ex	perinental value.	\$ [3].					
Group Group Group Group Dimethylamine 1 2 0 Dispropriamine 1 0 2 Dispropriamine 1 0 2	TIN S.	C N C	(E) N (E)	7.7	7.7)-) H.	(a) C-C (h	(a) C-C (c)	C-C (d)	C-C (e)	C-C (B	Calculated	Experimental	Relative Error
Dimethylamine Diethylamine Dipropylamine		÷ ;		, , ,								Total Bond	Total Bond	
	Croup	Croup	croup									Energy (eV)	Energy (eV)	ļ
		2	C	2	0	0	0	0	0	0	a	35.76895	35.765	-0.00012
				2	2	0	0	0	0	0	0	60,22930	60.211	-0.00030
		. ¢	٠.	, ,	-4	4		0	0	0	0	84.54470	84,558	0.00016
			, ,	+ 4	0	2	4	0	0	0	0	84.74648	84.846	0.00117
		۰ د	, ,					0	0	0	0	108,86010	108.872	0.00011
		• •	1 12	1 4	s 63	2	9	0	0	0	0	109.00522	109.106	0.00092

			-			<u> </u>	Т	T		1	_					
	Exp. θ (°)		112 (dimerkulanina)	107	111.8		(propane) 112 (propane) 113.8 (butane) 116.8	111.0 (butane) 111.4	(isopulane)			110.8	(Simple of the control of the contro	111.4	(isobutane)	(isobutane)
	(cal. <i>θ</i>		111.76	107.27	98 111		110.49	110.49	109.50	109,44	109.44	110.67	110.76	111.27	111.27	
	6,0															
	9 0	;			_											
	φ° ©						69.51	69.51		70.56	70.56					
0).	E_T (eV)		0	0	-I.85836	0			0			-1.85836	0	0	-1.85836	
- atom, msp³.A	20"		1.01756	0.95917	0.79816	1.15796			1.15796			0.81549	1.04887	1.04887	1.04887	
$E_T(atom$. 		0.75	0.75	-	0.75	() n		0.75			-	0.75	0.75	0.75	
ed. E_T is	້.			-	-	_			-				-	-	-	1
gle were u	<u>ن</u>		0.75	0.75	-	_			1			_	0.75	0.75	0.75	1
re preceding an	C ₂ Alon 2	0.03383	Eq. (15.117))	0.87418	0.79816	_			1			0.81549	17716.0	17716.0	177100	+
neters from th	C_2		0.91771	(Eq.	0.79816	0.86359			0.86359			0.81549	0.87495	0.87495	0.87495	+
Atom 2	Hybridization Designation	(Table 15.3.A)		z	29	н			E			25		E -		
ile calculatif	L'Castombre Atom 2		-14,53414	(Eq. (15.117))	-17.04640	ш			I			-10.08412 C	-14.82575 C,	-14.82575 C_	-14.82575 C _c	+
Atom I	Hybridization Designation	(Table 15.3.A)	2	7	29	7			7			25	\$	v	٧,	
2	Fredombe OF E	1 Mont 1	14.02.01	-14.53414	-17.04640	-15.75493			-15.75493		16.49412	C,	-15.55033 C_	-15,55033 C,	-15.55033 C,	
2c'	Terminal Alons (a)	4 0661	lonn't	3.8123	4.6260	3,4252			3.4252			4.7958	4.1633	4.1633	4.7958	
2c'	Bond 2 (a,)	2 79186		2.79186	2.79186	2.11106			2.09711			2.91547	2.11323	2,09711	2.90327	
2c'	7°	2.097(1.89621	2.79186	2.11106			2,09711			2.91547	2.91547	2.91547	2.90327	
Admits of Armits $2c'$ $2c'$ $2c'$ $6c'$ About $6c'$		ZHCN	(C = N (1) & (II))	(C-N(i)&(i))	(C-N (i) & (ii))	Maliylene ZHC _a H	25'27	ZC,C,H	HC,H	2C.C.H	70.00	isa C	L, C, L, H	$\angle C_a C_b H$ 150 C_a	∠۲,,۲, ۲, اما ۲,	ZC,C.C.

Table 15.80. The bond angle parameters of secondary amines and experimental values [1]. In the calculation

TERTIARY AMINES $(C_n H_{2n+3} N, n = 3,4,5...\infty)$

The tertiary amines, $C_n H_{2n+3} N$, have three C-N bonds to methyl or alkyl groups wherein C-N comprises a functional group. The alkyl portion of the tertiary amine may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise 5 methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in tertiary amines are equivalent to those in branched-chain alkanes.

The C-N group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. In tertiary amines, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \ eV$ (Eq. (15.25)), and the N AO has an energy of $E(N) = -14.53414 \ eV$. To meet the equipotential condition of the union of the C-N H₂-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the C-N-bond MO given by Eq. (15.116) is $c_2(C2sp^3HO \ to \ N) = 0.91140$.

As given in the Continuous-Chain Alkanes $(C_n H_{2n+2}, n=3,4,5...\infty)$ section, the energy of each $C2sp^3$ HO must be a linear combination of that of the CH_3 and CH_2 groups that serve as basis elements. Each CH_3 forms one C-C bond, and each CH_2 group forms two. Thus, the energy of each $C2sp^3$ HO of each CH_3 and CH_2 group alone is given by that in ethane, -0.72457~eV (Eq. (14.151)), and ethylene, -1.13379~eV (Eq. (14.511)), respectively. In order to match the energy of the component HOs and MOs for the entire molecule, the energy $E_{T_{alkaner}}\left(C-C,2sp^3\right)$ given as a linear combination of these basis elements is -0.92918~eV (Eq. (14.513)). In tertiary amines, the N binds to three $C2sp^3$ HOs and the corresponding $E_T\left(atom-atom,msp^3.AO\right)$ of each C-N-bond MO in Eq. (15.52) due to the charge donation

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from the C and N atoms to the MO is -0.92918~eV. It comprises a linear combination of the energy for a primary amine, -0.72457~eV and a secondary amine, -1.13379~eV.

The symbols of the functional groups of branched-chain tertiary amines are given in Table 15.81. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 5 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of tertiary amines are given in Tables 15.82, 15.83, and 15.84, respectively. The total energy of each tertiary amine given in Table 15.85 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.84 corresponding to functional-group composition of the molecule. The bond angle parameters of tertiary amines determined using Eqs. (15.79-15.108) are given in Table 15.86.

1.532 (propane) 1.531 (butane) 1.52750 0.68888

Table 15.81. The symbols of functional groups of tertiary amines.	Group Symbol	C-N	$C - H\left(CH_3\right)$	$C-H(CH_{\gamma})$	î = 1.	(8) (7-7)	(a) 2-3	(a)	(e) () - ()	(a) (-1)	€ (T)
Table 15.81. The symbols o	Functional Group	N.O	CH; group	CH2 group	CH	CC bond (n-C)	CC bond (iso-C)	CC bond (tert-C)	CC (iso to iso-C)	CC (t to t-C)	CC (t to iso-C)

Table 15.82.	The geometrical boa	nd parameters of ten	Table 15.82. The geometrical bond parameters of tertiary amines and experience to the connection of th	rimontol moluce [11					
Parameter	C ~ N Group	$C - H \left(CH_3 \right)$ Group	$(C-H)(CH_2)$	C-H Group	(; -(' (a) Group	('-('(b)) Group	C-(c)	(b) D~C	(a) 2-2
$a (a_0)$	1.96313	1.64920	1.67122	1,67465	7 17/100	1 12400		dinoin	dnon
c' (a.)	1 40117	104050			2,12437	7.17499	2.10725	2.12499	2.10725
	71101.1	0040.1	1.03533	1.05661	1,45744	1.45744	1 45164	1 45744	17.57
Bond							10100	1.43744	1,45164
Length $2c'(A)$	1.48288	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635
Fxn Rond		1 107	101						
Length	1.458 (trimethylamine)	(C - H propane)	(C~H propane)	1.122	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532
(2)	,	(C-H butane)	5	(isobutane)	1.531	1.531	1.531	1531	1.531
b,c $\{a_{b}\}$	1.37505	1 27795	1 30%00	1 20024	(outaile)	(outabe)	(butane)	(butane)	(butane)
,	0.71177	00000	105/31	1.27724	1.54616	1.54616	1,52750	1.54616	1.57750
	0.71372	0,03380	0.63159	0 63095	009890	00,00			2

2.10725

1.53635

Para	1,7		ı			1									
Dung	Arom	ET	ET	E	E_T	Final Total	franks	, final	Econtomi	$E(C2sp^3)$.0	b b	θ,	ď,	d,
		(eV)	(eV)	(eV)	(eV)	Energy	(a _o)	(a)	(eV)	(eV)	©	•	:©	(a,)	(a,)
		pond i	2 bond 2	S Duos	Bond 4	(eV)		5	riigi	Final	:	;	:	3	3
$N-(C_aH_3)_3$	ن."	-0.46459		0	0	-152.08028	0.91771	0.88983	-15.29034	-15.09948	83.37	96.63	40.00	1,50383	0.10271
$N-(C_aH_3)_3$	N	-0.46459	-0.46459	-0.46459	0		0.93084	0.83885	-16.21953		78.02	86'101	36.64	1.57525	0.17413
$N-(C_nH_2-)_3$	ڻ ^ع	-0.46459	-0.92918	0	٥	-153.00946	17716.0	0.83885	-16.21953	-16,02866	78.02	101.98	36.64	1.57525	0.17413
$N-(C_{\alpha}H_2-)_3$	N	-0.46459	-0.46459	-0.46459	0		0.93084	0.83885	-16.21953		78.02	101.98	36.64	1.57525	0.17413
$C-H$ (CH_3)	ز	-0.92918	0	0	0	-152,54487	17716.0	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H(CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	17716.0	0.81549	-16.68412	-16,49325	68.47	111.53	35.84	1.35486	0,29933
C-H (CH)	.)	-0.92918	-0,92918	-0.92918	٥	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_1G_1G_3H_2GH_2 - (C-C'(3))$	U"	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_c L_4 T H_1 - (C - C_c (a))$	ť	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R - H_2 C_s C_s \left(H_2 C_c - R^1 \right) H C H_2 - \left(C - C \cdot (b) \right)$	ر;	-0.92918	-0.92918	-0.92918	0	-154.40324	17710	0.77247	-17.61330	-17,42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2C_a(R^* - H_2C_a)C_k(R^* - H_2C_c)(H_2 - G_2)$ $(C - C_1(G))$	C,	-0.92918	-0 72457	-0.72457	-0.72457	-154.71860	17716.0	0.75889	-17.92866	-17.73779	48,21	131.79	21.74	1.95734	0.50570
$i k \alpha C_{\alpha} C_{\mu} \Big(H_{\alpha} C_{\nu} - R^{\mu} \Big) H C H_{\alpha} - (C - C^{\mu} (d))$	۲,	-0.92918	-0.92918	-0.92918	0	-154.40324	17716.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0,51388
$tertC_{\mu}(R-H_2C_{\mu})C_{\mu}(R^{\mu}-H_2C_{\nu})CH_2-$ $(C-C^{\mu}(C))$	۲,	-0.73457	-0.72457	-0.72457	-0.72457	-154,51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1,94462	0.49298
$tert'_{L}C_{L}(H_{2}C_{L}-R^{2})HCH_{2}-(C^{2}-C^{2}(f))$	۲.)	-0.72457	-0.92918	-0.92918	9	-154.19863	17716.0	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$lxaC_{\mu}(R'-H_2C_{\mu})C_{\mu}(R''-H_2C_{\nu})CH_2 - (C-C_{\nu}(f))$	1.5	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.83. The MO to HO intercept geometrical bond parameters of tertiary amines. R_iR_i , R^* are H or alkyl groups. E_r is E_r (atom – atom, msp². AC

Parameters	C-N	Parameters C-N (:H, C:H	CH ₂	C-H	C-C (a)	() C (P)	(c) (c)	C-C (d)	C-C (e)	C-C (f)
	dnoin	Group	Group	dinaio	dions	dingip	dinoip	dion	Cloub	dnorn
n.	_	m	2	1	1	1	1		ı	
n,	0	2	-	0	0	0	0	0	0	0
n,	0	0	0	0	0	0	0	0	0	0
ن ا	0.5	0.75	0.75	0.75	0.5	0.5	6.5	5.0	0.5	5'0
C ₂	_	-	_	1	-		1	Ţ	1	1
C,	-	-	-	ş-4	-	-	1	1	1	I
c_1	0.91140	0.91771	17716.0	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
5	0	0	1	1	0	0	0	1		0
J,	2	-	1	-	2	7	2	2	7	. 2
£,	0	3	2	1	0	0	0	0	0	0
(,,,	0.5	0.75	0.75	0.75	0.5	5,0	5.0	5.0	0.5	5'0
.,	-	-	I	ı	1	1	1	1	1	1
V, (eV)	-31.67393	-107.32728	-70.41425	-35,12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	9.71067	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T' (eV)	8.06719	32.53914	21.06675	10,48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V, (eV)	-4.03359	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3,45250	-3,45250
E(10 110) (eV)	-14.63489	-15.56407	-15.56407	-14,63489	-15.56407	-15.56407	-15,35946	-15.56407	-15,35946	-15.35946
ΔE_{H_2MO} (40 110) (eV)	-0.92918	0	0	0	0	0	0	0	0	0
Er (10 10) (eV)	-13.70571	-15.56407	-15.56407	-14,63489	-15,56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
$E_T(n_2no)$ (eV)	-31,63537	-67.69451	-49.66493	-31,63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31,63535
$E_r(atom - atom, msp^3, AO)$ (eV)	-0.92918	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_r(\iota \iota \sigma)$ (eV)	-32,56455	-67.69450	-49.66493	-31.63537	-33,49373	-33.49373	-33,08452	-33,49373	-33.08452	-33.08452
$\omega \left(10^{15} rad/s\right)$	18.1298	24.9286	24.2751	24,1759	9,43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	11.93333	16,40846	15.97831	(5.91299	6,21159	6.21159	10.19220	6.21159	6.29021	6.29021
\vec{E}_{D} (eV)	-0.22255	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{k\pi b}$ (eV)	0.12944	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0,35532 (Eq. (13.458))	0,12312	0.17978 [4]	0.09944	0.12312 [2]	0.12312 [2]	0.12312
\vec{E}_{mc} (eV)	-0.15783	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{m_{NN}}\left(eV ight)$	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T[imp]$ (eV)	-32.72238	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{minol}(c, \nu)$ in) (cV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489
E umad (c. 10 110) (cV)	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
E. (tirup) (eV)	3.45260	12,49186	7.83016	3.32601	4,32754	4.29921	3,97398	4.17951	3.62128	3.91734

Experimental
Total Bond
Energy (eV)
47.761
84.316
120.864 Calculated
Total Bond
Energy (eV)
47.83338
84.30648
120.77958 Table 15.85. The total bond energies of tertiary animes calculated using the functional group composition and the energies of Table 15.84 compared to the experimental values [3].

Formula Name C - C (a) C - C (b) C - C (c) C - C (d) C - C (e) C - C (f) C - C (f) C - C (f) 000 000 000 000 0 20 000

	Exp. θ (°)	110.9 (trimethylamine	107 (dimethylamine)	(propane) 112 (propane) 113.8 (butane) 110.8	(butane)	(Scondard)			110.8 Graphydaid	(soppliate)	111.4	(Isoburane)	(Isoburane)
	Cal. <i>θ</i>	110.48	108.44	110.49	110.49	109.50	109.44	109.44	110,67	110.76	111.27	111.27	
	θ ₂												7
	, (°)												
	ه (٥)			69.51	15.69		70.56	70.56					
	E_T (eV)	-1.85836	0			0			-1.85836	0	0	-1.85836	
om,msp'.AO	V	0.79340	1.15796			1.15796			0.81549	1.04887	1.04887	1.04837	
atom - at	٠ <u>.</u>	_	0.75			0.75	. 6	1		0.75	0,75	0.75	
L. E _T IS E ₁	హ	_	-			-				-	-	-	
le were used	౮	_	-			1			-	0.75	0.75	0.75	1
receding ang	C ₂ Atom 2	0.79340	-			-			0.81549	17716.0	17716.0	17716.0	
ers arom une p	C ₂ Atom I	0.79340	0.86359			0.86359			0,81549	0.87495	0.87495	0.87495	
Atom 2	Hybridization Designation (Table 15.3.A)	9	E			н			. 22	-		-	
Calculation	Contambe Atom 2	-17.14871	II			н			ري ري	-14.82575 C,	-14.82575 C_	-14.82575 C,	
Atom [Hybridization Designation (Table 15.3.A)	J	7			7			22	\$	8	5	
12	Combonite Or E Atom I	-17.14871	-15.75493			-15.75493		27,00,21	.10.08412 C,	-15.55033 C _a	-15.55033 C _k	-15.55033 C,	
2c'	Terninal Alons ($a_{\rm b}$)	4.6043	3.4252			3.4252			4.7958	4.1633	4.1633	4.7958	
2c'	Bond 2 (a _q)	2.80224	2.11106			2,09711			2.91547	2.11323	2.09711	2.90327	
2c'	۲")	2.80224	2.11106			2.09711			2.91547	2.91547	2.91547	2.90327	
Annual Angle $2c'$ $2c'$ $2c'$ R Annual		ZK.NC.	Methylene ZH(*, H	'כנ"נ."כ	ZC,C,H Mediwi	Н".)Н7	Z(,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	70.00	iso C,	ZC,C,H isn C,	$\angle C_s C_h H$ iso C_s	۲۲,۵,۲ رور ر	ZC,C,C,

Table 15.86. The bond angle parameters of tertiary amines and experimental values [1]. In the calculation of heta, the

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ALDEHYDES $(C_n H_{2n} O, n = 1, 2, 3, 4, 5... \infty)$

The alkyl aldehydes, $C_nH_{2n}O$, each have a HC=O moiety that comprises a C=O functional group and a CH functional group. The single bond of carbon to the carbonyl carbon atom, C-C(O)H, is a functional group. In addition to the C=O functional group, 5 formaldehyde comprises a CH_2 functional group. The alkyl portion of the alkyl aldehyde may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in aldehydes are equivalent to those in branched-chain alkanes.

The CH functional group was solved in the Hydrogen Carbide (CH) section except that E_{mog} is not subtracted since unpaired electrons are not created with fragmentation of the CH functional group of aldehydes. The CH_2 functional group of formaldehyde is solved in the Dihydrogen Carbide (CH_2) section except that the energy of each C-H MO is matched to the initial energy of the $C2sp^3$ HO (Eq. (15.25)). The C=O and C-C(O)H groups are solved by hybridizing the 2s and 2p AOs of each C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO or between two $C2sp^3$ HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl aldehydes, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)) and the O AO has an energy of $E(O) = -13.61806 \, eV$. To meet the equipotential condition of the union 25 of the C=O H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the C=O-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO to O) = 0.85395$. The unpaired electrons created by bond breakage of the double C=O bond requires that two times

the O2p AO magnetic energy E_{mag} (Eq. (15.60)) be subtracted from the total energy to give $E_{D}(Group)$ (eV) for C=O.

 $E_T \left(atom-atom, msp^3.AO \right)$ of the C=O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is -2.69893~eV which is an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the O atom. It is given as a linear combination of the energy contributions corresponding to a double bond, -1.13379~eV (Eq. (14.247)), and a triple bond, -1.56513~eV (Eq. (14.342)). The triple bond contribution includes the $C2sp^3$ HO electron of the C-H bond in addition to the pair involved directly in the double bond with O. 10 $E_T \left(atom-atom, msp^3.AO \right)$ of the C-C(O)H group is equivalent to that of an alkane, -1.85836~eV, where both energy contributions are given by Eq. (14.513). It is based on the energy match between the $C2sp^3$ HOs of the aldehyde. In order to match energy between the groups bonded to the C=O, electron-density is shared. Due to the interaction in the transition state between the groups based on the sharing, $C_{1o}=2C_1$ rather than $C_{1o}=C_1$ in Eq. (15.52) for the C-C(O)H bond.

The symbols of the functional groups of alkyl aldehydes are given in Table 15.87. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl aldehydes are given in Tables 15.88, 15.89, and 15.90, respectively. The total energy of each alkyl aldehyde given in Table 15.91 was calculated as the sum over the integer multiple of each $E_D(c_{troup})$ of Table 15.90 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl aldehydes determined using Eqs. (15.79-15.108) are given in Table 15.92.

Table 15.87. The symbols of functional groups of alkyl aldehydes.

Functional Group	Group Symbol
CH ₂ (formaldehyde) group	$C-H(CH_2)$ (i)
CH (aldehyde) group	CH (i)
C=O	C = O (i)
C-C(O)H	C-C(O)H
CH₃ group	$C-H$ (CH_3)
CH₂ (alkyl) group	$C-H\left(CH_{2}\right)$ (ii)
CH (alkyl)	C-H (ii)
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

					_			_	_		т-
Group	2 10705	2.101.2	1.45164	1.53635		1.532	(propane)	1.531	(butane)	1.52750	0.68888
C-C (e) Group	2 10725	4,1012	1.45164	1.53635		1.532	(propane)	1.551	(outane)	1.52750	0.68888
C-C (d) Group	2 12499	1 46744	1.45/44	1.54280		1.532	(propane)	L.J.J.	1 cació	1,34010	0.68600
C-C (e) Group	2.10725	1 45164	1.40104	1.53635		1.532	(propane)	(hutane)	1 52750	001201	0.68888
C - C (b) Group	2.12499	1 45744	11/22	1.54280		1.532	(propane)	(butane)	1 54616	01010:1	0.68600
C-C (a) Group	2.12499	1 45744		1.54280		1,532	(propane)	(butane)	1 \$4616	2701010	0.58600
	1.67465	1.05661		1.11827			(isobutane)		1.29924	2000	0.03095
$C-H(CH_2)$ (ii) Group	1.67122	1.05553		1.11713	1 107	(C-H mmm)	1.117	(C-H butane)	1,29569	0.63160	20,000
C ~ H (CH ₃) Group	1.64920	1.04856		1.10974	1 107	(C - H propere)	(3 II propance)	(C-H butane)	1.27295	0.63590	0.00.00
Group	2.04740	1.43087		1.51437		1.515	(acetaldehyde)		1.46439	18867 0	10000
Group	1.29907	1.13977		1.20628	1.208	(formaldehyde)	1.210	(acetaldehyde)	0.62331	0.87737	
	1.67465	1.05661		1.11827		1,128	(acetaldehyde)		1.29924	0.63095	
(- m (cm ₂) (t)	1.64010	1.04566		1.10668		1.116	(formaldehyde)		1.26354	0.63756	
	a (a ₀)	$c'(a_n)$	Bond	Length 2c' (A)	Exp. Bond	Length	گرگر		b,c (a_0)	ย	
	Group Group	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Group Group	Group Group C-H (CH, I) Group C-H (CH, I) Group C-H (II) Group C-C (a) Group C-C (b) Group C-C (c) Group C-C (d) Group C-C (e) Group </td <td>Group Group /td> <td> C - C (a) C - C (b) C - C (c) C - C (d) C - C (e) C - C (d) C - C (e) C -</td> <td>Group Group /td> <td> C</td> <td>$\begin{array}{c ccccccccccccccccccccccccccccccccccc$</td> <td>$\begin{array}{c ccccccccccccccccccccccccccccccccccc$</td> <td>$\begin{array}{c ccccccccccccccccccccccccccccccccccc$</td>	Group Group	C - C (a) C - C (b) C - C (c) C - C (d) C - C (e) C - C (d) C - C (e) C -	Group Group	C	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$

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Table 15.89. The MO to HO
Table 15.89. The MO to HO

Bond	Atom	_	t	,											
			1,1	L,	E_T	rinal 1 otal	Festival	finel	Ecautomis	$E(C2sp^3)$	θ,	θ	θ,	d.	ď
	_	(eV) Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	C2sp³	(a ₀)	(a ₀)	(eV) Final	(eV)	٥	• ①	·©	(a°)	(a)
()	+					(eV)				rınal					
$H(C(O) - H (CH_2) (i)$	ن	-1,34946	0	0	•	-152.96515	17716.0	0.84115	-16.17521	-15.98435	15.72	104.28	40.18	125314	0.20748
$-C_{\mu}H_{2}C_{\mu}(O)-H_{2}(CH_{2}(I)$	ڻ"	-1.34946	-0.92918	0		-153.89434	17716.0	0.79546	-17.10440	-16.91353	64.95	115.05	09 55	1 20245	20,000
$H_2C=0$	0	-1.34946	c	0	0		1,00000	0.84115	-16 17521		127.97	1 5	CO. C.		1,33064
$-C_nH_2C_s(H)=0$	0	-1.34946	0	0	0		1.00000	0 84115	-16.17521		127.77	12.13	15.00	0.52193	0.61784
$RH_2C_n - C_a(H)(O)$	ڻ	-1.34946	-0.92918	0	0	-153.89434	12210	0 79546	-17 10440	16.01257	12:24	43.65	1000	0.52193	0.61784
$H_3C_6 - C_a(H)(O)$	ئ	-0.92918	9	0	٥	-157 54487	0.01771	0.06250	12 75 100	cccleal-	PC.CC1	44.bb	63.78	0.57401	0.56576
$-C_bH_1 - C_s(H)(O)$:	-0.92918	X10400-	-		SOLET CS)	111110	eccoo n	-13.75493	-13.36407	1771	107.73	¥.17	1.69388	0,26301
(-H) (CH)	;	0.000		,	0	-133.47403	1//160	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
(6)	_	81676 0-		0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1,23564	0.18708
(=n (cn ₂) (n)		-0.92918	-0.92918	0	0	-153,47406	0.91771	0.81549	-16,68412	-16.49325	25'89	111.53	35.84	135486	0.29933
· (' – H (CH) (ii)	ij	-0.92918	-0.92918	-0.92918	0	-154.40324	17716.0	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42088	25220
$H_{\lambda}C''_{\lambda}C''_{\lambda}H_{\lambda}C''_{\lambda}$ (C'-('(a))	ن —	-0 92918	ů	0	D	-152,54487	17716.0	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_1^{\zeta}C_{\mu}^{\zeta}C_{\mu}H_2^{\zeta}CH_2^{\zeta} (\zeta'-\zeta''(a))$	ر.'	-0.92918	-0.92918	0	0	-153,47406	17716.0	0.81549	-16,68412	-16.49325	56.41	123.59	26.06	I 90xon	245117
$R-H_2C_{\mu}C_{\mu}(H_2C_{\mu}-R^{\mu})HCH_{\mu}$;														A LICENT
(((.(p))	۲. ه	-0 92918	-0.92918	81626'0-	5	-154.40324	17719.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0,51388
$R - H_2C_a(R^2 - H_2C_a)C_b(R^{11} - H_2C_a)CH_2 - (C - C^2(c))$. C,	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48,21	131.79	21.74	1.95734	0.50570
$lsio(",C_{\kappa}(H_2C_{\kappa}-R))HCH_2 - (C-C,C)$	C,	-0,92918	-0.92918	-0,92918	0	-154.40324	17716.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$ter(C_n(R'-H_2C_s)C_s(R''-H_2C_c)CH_2 - (C'-C'(e))$	C,	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1,94462	0.49298
$ler(C,C,k(H_2C_c-R)HCH_2-(C-C,f))$	C,	-0.72457	-0.92918	-0.92918	-6	-154,19863	17716.0	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$ksoC_{\sigma}(R'-H_2C_{\sigma})C_{\delta}(R''-H_2C_{\sigma})CH_2 - (C-C-C)$	۲,	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	17716.0	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
	:													_	_

Parameters	(7H ₂ (f)	CH (I) Group	dnou5 O≃3	C-C(O)H Group	CH ₃	CH, (ii) Groun	C - H (ii) Group	C-C(a) Group	C-C (b)	C - C (e) Group	C-C (d)	(e) 2-2	C-C(f)
n_1	2	-	2		3	2	-		-	-	4	from	- I
n,	-	0	0	0	2	-	0						1
, in	0	0	0	0	0	0					9	0 0	
.)	0.75	0.75	200			,		2	>		n	0	0
	C	67.0	co	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	5,0
۲۰2	-	-	1	1	1	1	1	ı	1	1	-	I	-
c_1	-		-	1	1	I	1	-	1	1		-	-
£,	0.91771	0.91771	0.85395	0.91771	17716.0	0.91771	0.91771	0.91771	0.91771	0.91771	17710	12210	122100
<i>c</i> ₃	-	0	2	0	0	ı	1	0	0	0		111700	111100
יט"	_	-	4	2	-	1	1	2	2	2	2		0
ć	2	1	0	0	æ	2		0	0	o	c	1 0	1 0
ر.	0.75	0.75	0.5	1	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	20
(,2,0	-		1	ı	1	1	-	1	-		-	-	} -
V, (eV)	-72.03287	-35.12015	-111.25473	-30.19634	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29 10112	-20 10112
V, (eV)	26.02344	12.87680	23.87467	9,50874	38.92728	25.78002	12.87680	9.33352	9,33352	9.37273	9 33352	9 37773	0 37773
T (eV)	21.95990	10.48582	42.82081	7.37432	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6 77464	005069	005009
V, (eV)	-10.97995	-5.24291	-21.41040	-3.68716	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
L. L. v. 110) (eV)	-14.63489	-14,63489	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15,56407	-15.35946	-15.56407	-15,35946	-15.35946
Δε _{μ, λεο} (λο. πο) (eV)	0	0	-2.69893	0	0	0	0	0	0	0	0	0	0
$E_{T}(w) (eV)$	-14.63489	-14.63489	2.69893	-14.63489	-15.56407	-15,56407	-14.63489	-15.56407	-15,56407	-15.35946	-15,56407	-15.35946	-15 35946
$E_T(u, un)$ (eV)	-49.66437	-31.63533	-63.27074	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31 63535	-31 63535
$E_T(atom - atom, msp^3, AO)$ (eV)	0	0	-2.69893	-1.85836	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{\gamma}(sw)$ (eV)	-49,66493	-31.63537	-65.96966	-33.49373	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33,49373	-33.08452	-33.08452
@ (1013 rad 1.8)	25.2077	24.1759	59.4034	23.3291	24.9286	24.2751	24.1759	9.43699	9,43699	15.4846	9.43699	9.55643	9.55643
E_{κ} (eV)	16.59214	15.91299	39.10034	15.35563	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6,21159	6.29021	6.29021
En (eV)	-0.25493	-0.24966	-0.40804	-0.25966	-0.25352	-0.25017	-0,24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0 16416
E_{Kirk} (eV)	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.21077	0.13800 [26]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
$E_{uc}(eV)$	-0.07727	-0.07200	-0.30266	-0.19066	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0 10260
E_{neg} (eV)	0.14803	0,14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
F. (Group) (eV)	-49.81948	-31.70737	-66.57498	-33.68439	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
L situal (c. 30 110) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
E metral (c. 10 110) (eV)	-13.59844	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
L. D. triman (CV)	7.83968	3.47404	7.80660	4.41461	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3 91734

										Contraction of the contraction o							
romanta	Name	('H ₂ (i)	\mathbb{G}_{H}	0=0	C-C(O)H	('H',	('H', (ii)	CH (ii)	C-C (a)	C-C(b)	(6)	C-C (d)	C-C (e)	C-C (f)		Experimental	Relative Error
		Group	dnos	Group	Group							,	;		Total Bond	Total Bond	
	Formaldelivde		0	-		10			4							Energy (eV)	
C.H.O	Aestaldehyde		÷		-				0 1	0		0	0	0		15,655	0.00056
	Proparal		• •					0 1	0	0	0	0	0	0		28.198	0.00039
	Butanal	: 0					- ,	۰.	- (0	0	0	0	0		40,345	0,0000
	Isobutanal		. –				v c	5 -	7 :	0	0	0	0	0		52.491	-0.00022
	Pentanal					7 -	٠,		۰ -	7	0	-	0	0		52.604	0.00001
	Heptanal	0	-				n 14	> •	n 1	.	0	0	0	0		64.682	0,00034
	Octanal			٠			n (-	0 1	0	0	0	0	0		88.942	-0.00038
	2-Ethylhexanal	. 0				۰, ۲	s -	- c	s.	0 (0		0	0		101.179	0.00045
						7	†		•	'n	0	6	0	_		101 350	20000

	Exp. θ (°)		formald-shades	115,3	(acceduting)	(acctaldehyde)	(propane)	112 (propane) 113.8 (butane) 110.8	(isobutanc)	111.0 (butane) 111.4	109.8	(acctaldenyde)		110.8	formmone)	111.4	(Isobutane)	(isobutane)
	Cal. <i>θ</i>		116.87	115.52		07.621	108.44	110.49		110.49	109.50	+	109.44	110.67	110.76	111.27	11 33	
	θ' (O)	:																1
	ι _θ (ε)												1					\top
	θ [*] ©							69.51		69.51		20.02	200	DCD/				
7).	E_T (eV)			0	7,557	0.000.1	3				0			-1.85836	0	0	-1.85836	
ים. לפווויווווו	2,		1.20470	1.06267	0.83477	1.15796					1.15796			0.81549	1.04887	1.04887	1.04887	
- 1/2/2	<i>5</i>		0.75	0.75	-	0.75					0.75				0.75	0.75	0.75	
2	ڻ -		-	-	-	-					1			I	-		-	
	<u>ئ</u>		-	0,75		_					1			-	0.75	0.75	0.75	
3	c ₂ Λίοπι 2			17710	0.85395	(Eq. (15.114))					-			0.81549	17716.0	17716.0	0.91771	
	c_2 Atom [0.83008	0.86359	0.81549	0.86359				·	0.86359			0.81549	0.87495	0.87495	0.87495	
41000	Atom 2 Hybridization Designation	(Table 15.3.A)	x	_	0	#					Ξ			я		_	-	
ľ	Contouring Atom 2		×	-14.82575 C ₆	-13,61806	=					д		-	-16.68412 C,	-14.82575 C _b	-14.82575 C_	-[4.82575	ï
Arom 1		(Table 15,3,A)	<u>~</u>	7	25	7					7			22	٠,	20	2	
,	Atom I		-16,39089	-15.75493 C.	-16,68412	-15.75493					-15.75493			-16.68412 C _b	-15.55033 C.	-15.55033 C _b	-15.55033 C,	,
300	Terminal Atons (a _n)		3.5637	4.2269	4.5826	3,4252					3.4252	-		4.7958	4.1633	4.1633	4.7958	
1,70	(a _a)		2.091.32	2.11323	2.27954	2.11106					2.09711			2.91547	2.11323	2,09711	2.90327	
201	Bond I	2,000	75160.7	2,86175	2.86175	2,11106					2.09711			2.91547	2.91547	2.91547	2.90327	
Akmins of Angle 2, 2, 2, 1, 2, 1, 2, 1, 2, 1, 2, 1, 2, 1, 2, 1, 2, 1, 2, 1, 2, 1, 2, 1, 3, 1, 3, 1, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3,		н".ж7	$(C_{\sigma}H_{2}(O)$ (i))	$ZC_{n}C_{n}H$ $RC_{n}(H) = O$	0°.5'.57	Methydone ZHC _u H		כ"כ"כ"		ZC, C, H	Н".ЭН7	לג"כ"כ	ZC,C,H	مرد"ر" انت د"	∠C',C',H iso C',	کر:'ر' <i>H</i> نه <i>د</i> ''	<i>کر</i> در کر اور اور اور اور اور اور اور اور اور او	70,07

KETONES $(C_n H_{2n} O, n = 1, 2, 3, 4, 5...\infty)$

The alkyl ketones, $C_nH_{2n}O$, each have a C=O moiety that comprises a functional group. Each of the two single bonds of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. The alkyl portion of the alkyl ketone may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in ketones are equivalent to those in branched-chain alkanes.

The C=O and C-C(O) groups are solved by hybridizing the 2s and 2p AOs of each C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO or between two $C2sp^3$ HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ketones, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489~eV$ (Eq. (15.25)) and the O AO has an energy of E(O)=-13.61806~eV. To meet the equipotential condition of the union of the C=O H_2 -20 type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the C=O-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO~to~O)=0.85395$. The unpaired electrons created by bond breakage of the double C=O bond requires that two times the O2p AO magnetic energy E_{mag} (Eq. (15.60)) be subtracted from the total energy to give $E_D(Group)$ (eV) for C=O.

As in the case with aldehydes, $E_T(atom-atom, msp^3.AO)$ of the C=O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-2.69893 \ eV$ which is an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the O atom. It is given as a linear combination of

the energy contributions corresponding to a double bond, $-1.13379 \, eV$ (Eq. (14.247)), and a triple bond, $-1.56513 \, eV$ (Eq. (14.342)). The triple bond contribution includes the $C2sp^3$ HO electron of the C-C(O) bond in addition to the pair involved directly in the double bond with O. Consequently, $E_T(atom-atom, msp^3.AO)$ of the C-C(O)-bond MO is $-1.44915 \, eV$, corresponding to the energy contributions of the two $C2sp^3$ HOs to the single bond that are equivalent to those of methyl groups, $-0.72457 \, eV$ (Eq. (14.151)). Since there are two C-C(O) bonds in ketones versus one in aldehydes, $C_{1o}=C_1$ in Eq. (15.52) for each C-C(O) ketone bond.

The symbols of the functional groups of alkyl ketones are given in Table 15.93. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.55)) parameters of alkyl ketones are given in Tables 15.94, 15.95, and 15.96, respectively. The total energy of each alkyl ketone given in Table 15.97 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.96 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl ketones determined using Eqs. (15.79-15.108) are given in Table 15.98.

Table 15.93. The symbols of functional groups of alkyl ketones.

Table 13.33. The symbols of	Tulloudian groups of any i kele
Functional Group	Group Symbol
C=O	C = O
C-C(O)	C-C(O)
CH₃ group	$C-H\left(CH_{3}\right)$
CH ₂ group	$C-H$ $\left(CH_{2}\right)$
ĆH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

C-C (f) Group	2.10725	1.45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	000000
C-C (e) Group	2.10725	1.45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0,0000
C-C (d) Group	2.12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	00200
C-C (c) Group	2.10725	1.45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	000000
C - C (b) Group	2.12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	. 00000
C-C (a) Group	2.12499	1.45744	1,54280	1.532 (propane) 1.531 (butane)	1.54616	00,00
C-H Group	1.67465	1.05661	1.11827	1.122 (isobutane)	1.29924	20000
(CH_3) $C-H(CH_2)$ oup	1.67122	1.05553	1.11713	1.107 (C - H propane) 1.117 (C - H butane)	1.29569	23.63
$C - H (CH_3)$ Group	1.64920	1.04856	f.10974	$\begin{array}{c} 1.107\\ (C-H \text{ propane})\\ 1.117\\ (C-H \text{ butane}) \end{array}$	1.27295	00200
Parameter $C = O$ $C - C(O)$ $C - H$ Group Group Group	2.04740	1,43087	1.51437	1.520 (acetone) 1.518 (2-butanone)	1.46439	20000
C = 0 Group	1,312172	1.14550	1.21235	(acetone) (1.219 (2-butanone)	0.64002	
Parameter	a (a ₀)	c' (a _b)	Bond Length 2c' (A)	Exp. Bond Length (A)	h,c (a)	

Table 15.95. The MO to HO intercept geometrical band parameters of alkyl ketones.	trical bond	parameters of al		R,R',R'' are H or alkyl groups. E_r is $E_T \left(atom - atom, msp^3, AO \right)$	alkyl groups. 1	S_T is E_T (atom-	– atom, msp³.A	<i>to</i>).						i !	i
Bond	Atom	E _T	E,	E,	E _T	Final Total	Finned	, final	Ecatomb	$E(C2sp^3)$.0	l _θ	θ,	d,	d ₂
		(eV) Bond f	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C2sp³ (eV)	(a_o)	(a)	(eV) Final	(eV) Final	©	(0)	(•)	(a _o)	(a_o)
$R'C_rH_2(RC_bH_2)C_a=0$	0	-1,34946	0	0	0		1.00000	0.84115	-16.17521		136.09	43.91	65.72	0.53955	0,60595
$R'C_cH_2(RC_bH_2)C_s = O$	ڻ:	-1.34946	-0.72458	-0.72458	0	-154.41430	0.91771	0.77199	-17.62437	-17.43350	133.02	46.98	98.19	0.61878	0.52672
$H_{\gamma}C_{\nu}-C_{\sigma}(O)(R')$	نځ	-0.72458	0	0	0	-152.34026	0.91771	0.87495	-15,55033	-15.35946	73.62	106.38	34.98	1.67762	0.246675
$RH_1C_r - H_2C_s - C_s(O)(R^r)$	ť	-0.72458	-0,92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28865	67.40	112.60	31,36	1.74821	0.31734
$C-H$ (CH_3)	ù	-0.92918	0	0	0	-152,54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H$ (CH_2)	i	-0.92918	-0.92918	0	0	-153,47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
C – H (CH)	i	-0.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31,37	1.42988	0.37326
$H_3C_aC_aH_2CH_2 - (C-C_aG_a)$	U [*]	-0.92918	0	0	0	-152,54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_6H_3CH_3-$ (C - C (a))	ΰ,	-0.92918	-0.92918	0	0	-153,47406	17716.0	0.81549	-16.68412	-16,49325	56.41	123.59	26.06	1.90890	0.45117
$R = H_2C_p(H_2C_p - R)HCH_2 - (C - C (b))$	73	-0.92918	-0.92918	-0,92918	G	-154,40324	17710.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2C_a(R^* - H_2C_a)C_h(R^* - H_2C_c)CH_2 - (C - C^*(0))$	ئ	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	17716.0	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_aC_b(H_2C_b - R^*)HCH_2 - (C-C^*(d))$	ť	.0.92918	-0.92918	-0.92918	0	-154 40324	0.91771	0.77247	-17.6[330	-17,42244	48.30	131.70	21.90	1.97162	0.51388
$Ier(C_{\mu}(R^{\mu} - H_{\underline{\mu}}C_{\mu})C_{\lambda}(R^{\mu} - H_{\underline{\mu}}C_{\mu})CH_{\underline{\mu}} - (C - C^{\mu}(\mathbf{e}))$	۲,	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0,76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0,49298
$ler(C,C_{k}(H_{2}C_{c}-R^{\prime})HCH_{2}-(C-C^{\prime}(f))$	ť	-0.72457	81626'0~	-0.92918	-0	-154.19863	17710	0,78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0,47279
$IsoC_{a}(R'-H_{2}C_{a})C_{b}(R''-H_{2}C_{a})C'H_{2} (C-C'(f))$	ڻ	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17710	0.76765	-17,92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.90. The energy parameter	S (cv) or runcholl	al groups or any	ACIDINO.		-	1000	300	1300	1700	(9)	(P)
Parameters $C = O C - C(U) C_{\alpha}$ C_{α}	0=0	(O) 2 - C Group	CH,	CH ₂	dnos Group	Group	Group	Group	Group	Group	Group
	2	-	3	2	-	-	1	1	-	1	1
	0	c	2		0	0	0	0	0	0	0
	٥	, c	0	0	0	0	0	0	0	0	0
£ 0	0.5	0.5	0,75	0.75	0.75	0.5	0.5	0.5	5.0	6.5	0.5
.5	-	-		_	-	1	1	1	1	1	1
2		-	-	-	-	1		1	1	1	1
	0.85395	17716.0	0.91771	17716.0	17716.0	0.91771	177160	17716.0	17716.0	17716.0	0.91771
c,	2	0	0	-	I	0	0	0	1	1	0
, C,	4	2	_	1	-	2	2	2	2	2	2
, t	0	0	3	2	-	0	0	0	0	0	0
C.	0.5	-	0.75	0.75	0.75	0.5	. 0.5	0.5	6.0	0.5	6.5
	-	-	_	1	-		1	1	1	1	-
V, (eV)	-109.17602	-30.19634	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	23.75521	9.50874	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9,37273	9.37273
T (eV)	41.60126	7,37432	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_ (eV)	-20.80063	-3.68716	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E (10 10) (eV)	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
ΔΕ _{11,210} (.20 110) (eV)	-1.34946	. 0	0	0	0	0	0	0	0	0	0
E_(.io'no) (eV)	1.34946	-14.63489	-15,56407	-15.56407	-14.63489	-15.56407	-15,56407	-15,35946	-15.56407	-15.35946	-15.35946
$E_r(u_s, \omega)$ (cV)	-63.27071	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31,63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{\tau}(atom - atom, msp^3.AO)$ (eV)	-2.69893	-1,44915	0	0	0	-1.85836	-1,85836	-1.44915	-1.85836	-1.44915	-1.44915
E_(320) (eV)	-65.96966	-33.08452	-67.69450	-49,66493	-31,63537	-33.49373	-33,49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (10 ¹⁵ rad / s)	57.0928	16.4962	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E. (eV)	37,57947	10.85807	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
E. (eV)	-0.40003	-0.21568	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Extra (eV)	0.21462	0.14655	0.35532	0.35532 (Eq. (13.458))	0.35532 (Fo (13.458))	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
(eV)	-0.29272	-0.14240	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E. (eV)	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\tau}(i_{map})$ (cV)	-66,55510	-33.22692	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E men (c. 40 110) (eV)	-14,63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14,63489	-14.63489
E min (c. 10 10) (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(imp)$ (eV)	7.78672	3.95714	12.49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.97. The total bond energies of alkyl ketones calculated using the functional group composition and the energies of Table 15.96 compared to the experimental values [3]. The magnetic energy E_{asc} that is subtracted from the weighted sum of the E_{b} (and)

Formula	Name	0=0	(O)2~2	H.C	H.J	HJ	(a)	C-C (a) $C-C$ (b) $C-C$ (c) $C-C$ (d) $C-C$ (e)	(e) C-C	C-C (d)	C-C (e)	C-C (B)	Ŀ	Calculated	Experimental	Relative Error
		3 (·	6,5	17.7	;							No.	Total Bond	Total Bond	
		dinoin	dnos											Energy (eV)	Energy (eV)	
C.H.O	Acetone	_	2	7	0	0	0	0	0	0	0	0	0	40,68472	40,672	-0.00031
C.H.O	2-Butanone	_	C)	61		0	-	0	0	0	0	0	0	52.84242	52.84	•0.00005
	2-Pentanone	_	7	7	27	0	7	0	0	0	0	0	٥	65.00012	64.997	-0.00005
	3-Pentanone	_	· C1	7	•	0	CI	0	0	0	0	0	0	65.00012	64,997	-0.00005
	3-Methyl-2-hutanone		7	m	0		0	7	0	0	0	ø	o	65,10101	65.036	-0.00099
	2-Hexanne		2	7	7	0		0	0	0	0	0	0	77.15782	77.152	-0.00008
	3-Hexanone		1 61	1 12	1 177	0	. (*)	0	0		0	0	0	77,15782	77.138	-0.00025
	2-Methyl-3-pentanone		1 7	m		_		7	0	0	0	0	0	77,25871	77.225	-0.00043
	3 3-Dimethyl-2-butanone	-	2	4	0	0	0	0	e	0	0	0	71	77.29432	77,273	-0.00028
	3-Hentanone		1 74	7	4	0	4	0	0	0	0	0	0	89,31552	89.287	-0.00032
	4-Hentanone	-	71	0	4	0	4	0	0	0	0	0	0	89,31552	89,299	-0.00018
C.H.	2 2-Dimethol-3-nentanone	_	C	4	_	0	_	0	m	0	0	0	7	89.45202	89.458	0.00007
0.11.0	2.4-Dimethyl-3-nentanone		7	4		6	0	4	0	0	0	0	0	89.51730	89.434	-0.00093
C.H.O	2.2.4-Trimethyl-3-nentatione		r.	٠	0	-	0	7	en	0	0	0	7	101,71061	101,660	-0.00049
0"H"	2-Nonanone		· Cl	7	• •	0	9	0	0	0	0	0	0	113,63092	113,632	0.00001
C.H.C	S-Nonanone		2	7	9	0	9	0	0	0	0	0	0	113,63092	113,675	0.00039
	2 6 Dimethyl 4 hontonene	-	r	4	,	,	C	9	0	0	0	0	0	113.77604	113 807	0,00027

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Exp. θ (°)	116.0 (acetone)	113.5 (2-butanaone)	121.9 (2-butanaone)	107 корале)	112 (propane) 113.8 (butane) 110.8 (isobutane)	111.0 foutane) 111.4 obutane)	108.5 (acetone)			(Isobutane)		(isobutane)	(isobutane)	
			-						_					_
Cal. <i>(</i> °)	115.77	113.71	122.07	108.44	110.49	110.49	109.50	109.44	109.44	110.67	110.76	111.27	111.27	107.50
(o)														_
(e)		·												
(e)					15.69	69.51		70.56	70.56					72.50
E_T (eV)	-1.85836	-1.85836	-1,44915	٥			0			-1.85836	0	0	-1.85836	
ۍ د	0.81549	0.81549	0.86445	1.15796			1.15796			0.81549	1.04887	1.04887	1.04887	
دا	1	1	1	0.75			52.0			-	0.75	0.75	0.75	
\mathcal{C}_2	1	_	1				1				_	-	1	
c ₁	1	-	-	1			-		-		0.75	0.75	0.75	
C ₂ Atom 2	0.81549	0.81549	0.85395 (Eq. (15.114))	1			-		i	0.81549	17716.0	17216'0	17716.0	
C ₂ Atom i	0.81549	0.81549	0.87495	0.86359			0.86359			0.81549	0.87495	0.87495	0.87495	
Atom 2 Hybridization Designation (Table 15.3.A)	2.5	25	0	н			ж			25	_	_		
Econtambre Atom 2	-16.68412 C	-16.68412 C_	-13.61806	ж			æ			-16.68412 C _e	-14.82575 C _k	-14.82575 C_	-14.82575 C	
Atom I Hybridization Designation (Table 15.3.A)	25	25	\$	7			7			25	vs	vs	'n	
Eradonic Ann 1	-16.68412 C,	-16.68412 C ₂	-15.55033	-15.75493			-15.75493			-16.68412 C,	-15.55033 C_	-15.55033 C,	-15.55033 C,	
2c' Terminal Atoms (a _p)	4.8477	4.8374	4.5166	3,4252			3.4252			4.7958	4.1633	4.1633	4.7958	
2c' Band 2 (a ₀)	2.86175	2.86175	2.29100	2,11106			2,09711			2.91547	2.11323	2.09711	2.903.27	
2c' Bond 1 (a _n)	2.86175	2.91547	2.86175	2,11106			2.09711			2.91547	2.91547	2.91547	2.90327	
Atoms of Angle	לכי"נ"(O)כ ^י	ZC,C,C,(0)	0'3'37	Methylone ZHC, H	່ ວ່າວ້ວ7	H,C,C,H	Methyd ZHC "H	לכ"כ"כ	H,2,22	رک ^ا در 'ر نه در'	LC,C,H 150 C,	"." (", H "." (", H	العداد" مراثر"د"	ZC,C,C,

CARBOXYLIC ACIDS $(C_n H_{2n} O_1, n = 1, 2, 3, 4, 5...\infty)$

The alkyl carboxylic acids, $C_nH_{2n}O_2$, comprise a C=O functional group, and the single bond of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. Formic acid has a HC=O moiety that comprises a more stable C=O functional group and a CH functional group. All carboxylic acids further comprise a C-OH moiety that comprises C-O and OH functional groups. The alkyl portion of the alkyl carboxylic acid may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The CH functional group was solved in the Hydrogen Carbide (CH) section except that the energy of the C-H MO is matched to the carbon-atom contribution to $\Delta E_{H_2MO}(AO/HO)$ and $E_T(atom-atom,msp^3.AO)$ of the C-O group. The alkyl carboxylic acid C=O and C-C(O) groups are equivalent to those given in the Aldehydes section except that \overline{E}_{Kwih} is that of a carboxylic acid. The formic acid C=O group is solved equivalently to that of the alkyl carboxylic acid group, except that $\Delta E_{H_2MO}(AO/HO)$ and $E_T(atom-atom,msp^3.AO)$ correspond to a 25% increase in the donation of charge density from the orbitals of the atoms to the C=O MO due to the presence of a H bound to the carbonyl carbon. Also, \overline{E}_{Kwih} is that corresponding to formic acid. The C-O and OH groups are equivalent to those of alkyl alcohols given in the corresponding section except that the energy of the C-O MO is matched to that of the C=O group and \overline{E}_{Kwih} is that of a carboxylic acid. $\Delta E_{H_2MO}(AO/HO)$ of the C-O group is equal to $E_T(atom-atom,msp^3.AO)$ of the alkyl C=O group in order to match the energies of the corresponding MOs.

As in the case with aldehydes and ketones, $E_T(atom-atom, msp^3.AO)$ of the C=O-bond MO in Eq. (15.52) of alky carboxylic acids due to the charge donation from the C and O

atoms to the MO is -2.69893~eV which is an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the carbonyl O atom. It is given as a linear combination of the energy contributions corresponding to a double bond, -1.13379~eV (Eq. (14.247)), and a triple bond, -1.56513~eV (Eq. (14.342)). The triple bond contribution includes the energy match of the carbonyl $C2sp^3$ HO electron with the O of the C-O-bond MO in addition to the pair involved directly in the double bond with the carbonyl O.

 $E_T \left(atom - atom, msp^3.AO \right)$ of the formic acid C = O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is -3.58557~eV. This is also an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the carbonyl O atom. It is given as a linear combination of the energy contributions corresponding to a triple bond, -1.56513~eV (Eq. (14.342)), and a quadruple bond, -2.02043~eV (Eqs. (15.18-15.21) with s=4)) where the bond order components are increased by an integer over that of alkyl carboxylic acids due to the presence of a H bound to the carbonyl carbon.

 $E_T \left(atom - atom, msp^3.AO \right)$ of the carboxylic acid C - C(O) group is equivalent to that of alkanes and aldehydes, -1.85836~eV, where both energy contributions are given by Eq. (14.513). It is based on the energy match between the $C2sp^3$ HOs of the carboxylic acid. As in the case of aldehydes, $C_{1o} = 2C_1$ in Eq. (15.52).

 $E_T \left(atom-atom, msp^3.AO \right)$ of the carboxylic acid C-O group is equivalent to that of alkyl alcohols, -1.85836~eV. It is based on the energy match between the O AO and the $C2sp^3$ HO of a methylene group (the maximum hybridization for a single bond) where both energy contributions are given by Eq. (14.513). $E_T \left(atom-atom, msp^3.AO \right)$ of the C-O group matches that of the C-C(O) group.

The symbols of the functional groups of alkyl carboxylic acids are given in Table 15.99. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acids are given in Tables 15.100, 15.101, and 15.102, respectively. The total energy of each alkyl carboxylic acid given in Table 15.103 was calculated as the sum over the integer multiple of each E_D (Group) of Table 15.102 corresponding to functional-group composition of the molecule. For each set of unpaired

electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl carboxylic acids determined using Eqs. (15.79-15.108) are given in Table 15.104.

Table 15.99. The symbols of functional groups of alkyl carboxylic acids.

Functional Group	Group Symbol
CH (formic acid) group	C-H (i)
C-C(O)	C-C(O)
C=O (formic acid)	C = O (i)
C=O (alkyl carboxylic acid)	C = O (ii)
(O)C-O	C-O
OH group	OH
CH₃ group	$C-H\left(CH_{3}\right)$
CH ₂ group	$C-H$ $\left(CH_{_{2}}\right)$
CH (alkyl) group	C-H (ii)
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

_		_				_			_	_
() J-J	Group		2.10725	1.45164	1.53635		1,532 (propane) 1,531	(butane)	1.52750	0.68888
(0)	Group	•	2.10725	1.45164	1.53635		1.532 (propane) 1.531	(butane)	1.52750	0,68888
(9)	Group Group	•	2.12499	1,45744	1.54280		1.532 (propane)	(butane)	1.54616	00989'0
300	Gotto Group		2.10725	1,45164	1.53635		1.532 (propane)	(butane)	1.52750	0.68888
- 200	Group		2.12499	1.45744	1.54280		1.532 (propane)	(butane)	1.54616	0.68600
1300	Group Group	1	2.12499	1,45744	1.54280		1.532 (propane)	(butane)	1.54616	0.68600
100	Growin	dono	1.67465	1.05661	1.11827		1 122	(isognane)	1.29924	0,63095
<u> </u>	$C-H(CH_1)$	Group	1.67122	1.05553	1.11713	1 107	(C - H propane)	1.117 (C~H butane)	1.29569	0.63159
	$C-H(CH_3)$	Group	1.64920	1.04856	1.10974	1.104	(C-H propage)	1.117 (C~H butane)	1.27295	0.63580
	НО	droup	1.26430	0.91808	0.971651		0.972		0.86925	0.72615
lidi varuca i i I-	0-0	Group	1.73490	1.31716	1.39402		1.393 (methyl	formate)	1,12915	0.75921
31	C=0 (ii)	croup	1.29907	1.13977	1,20628		1.214	(acetic acid)	0.62331	0.87737
ZIKYI CATOOXYIIC AC	(j) 0=2	Group	1,290799	1.13613	1,20243		1.202	(formic acid)	0.61267	0.88018
Table 15.100. The geometrical bond parameters of girkyl catuoxylic actus and experim	(a)D-D	Group	2.04740	1.43087	1,51437		1.520	(acetic acid)	1 46439	0.6987
The geometrical b	() H-)	Group	1.61341	1.03711	1.09763		1.097		103561	0.64281
Jable 15, 100.	Parameter	_	a (a,)	c, (a,)	Bond Length	(,,)	70)E	(0) 9, 9	6 6

	$\begin{pmatrix} d_1 & d_2 \\ \langle a_b \rangle & \langle a_o \rangle \end{pmatrix}$	2 0.55182 0.36625	8 1.14765 0.16950	4 1,26386 0.05329	8 1.14765 0.16950	0 1.29138 0.02578	5 0.53635 0.59978	12 0.58561 0.55053	11 0,52193 0,61784	16 0.62072 0.51905	99 1,30373 0,26662	17 1.85002 0.41915	8866971	58 1.76270 0.33183	18 1.23564 0.18708	34 1.35486 0.20933	17 1.42988 0.37326	30.08 1.83879 0.38106	26.06 1,90850 0.45117	21.90 1.97162 0.51388	21.74 1.95734 0.30370	21.90 1.97162 0.51388	22 66 1.94462 0.4929R	24.04 1.92443 0.47279	-
	(e) (e)	G4.91 G4.12	78.68 48.58	86.06 43.24	78 G8 48.58	88.04 41.90	42.90 65.45	14.76 63.02	42.73 66.31	46.53 61.46	110.11	123.75 25.37	107.73 34.17	114.01 30.58	102.51 41.48	111.53 35.84	31.37	116.18 30	123.59 36	131.70 21	131.79 21	131.70 21	129.96	HZ 22.721	_
	θ, (₀)	115.09	101.32	93.94	101.32	91,96	137.10	135.24	72.721	133.47	69,83	\$6,25	72.27	65.99	77.49	68.47	61.10	63.82	56,41	48.30	48.21	48.30	50.04	52.78	
	$E(C2sp^3)$ (eV) Final			-17.35685		-17 84271		-17.35685		-17.84271	-17.35685	-17 84271	-15.56407	-16,49325	-15.56407	-16 49325	-17.42244	-15.56407	-16.49325	-17.42244	-17.73779	-17,42244	-17,73779	-17.21783	
	E _{Control} (eV) Final	-15.75493	-15.75493	-17.54772	-15.75493	-18.03358	-16.61853	-(7.54772	-16 17521	-18,03358	-17.54772	-18.03358	-15,75493	-16.68411	-15,75493	-16,68412	-17 61330	-15.75493	-16.68412	-17.61330	-17.92866	-17,61330	-17.92866	-17,40869	
$om, msp^3.AO$.	$\binom{r_{\rm ford}}{(a_{\rm o})}$	0.86359	0.86359	0.77536	0.86359	0,75447	0.81871	0.77536	084115	0.75417	0.77536	0,75447	0.86359	0.81549	0.86359	0.815.0	74277.0	0.86359	0.81549	0.77247	0.75849	0.77247	0,76765	0.78155	
$E_{\tau}(atom - ate$	(a,)	1.00000	1 00000	17716.0	000001	0.91771	000001	14416.0	1.00000	17710	17716.0	17716.0	122160	17710.0	0.91771	17710,0	17716.0	17716-0	0.91771	17716.0	0.91771	17716-0	17716.0	0.91771	
groups. E, is	Final Total Energy ('2xp')			-154.33765		-154.82352		-154.33766		-154.82352	-15433766	-154 82352	-152.54487	-153,47405	-152.54487	-153,4741%	-154,40324	-152,54487	-153,47406	-154,40324	-154,71860	+154,40324	-154,51399	-154,19%63	
are H or alkyl	(eV) Bond 4	c	С	c	5	С	Ü	c	0	0	D	0	0	٥	0	0	0	0	0	0	-0.72457	0	-0.72457	đ	
parameters of alkyl carboxylic acids. R, R', R" are H or alkyl groups. E, is $E_r(atom-atom,msp^3.AO)$	E ₇ (eV) Bond 3	0	c	c	0	-0.92918	o	c	0	-0.92918	c	A.92918	0	=	=	e	-0.92918	0	c	4,929.18	-0,72457	-0.92918	-0.72457	816 <u>2</u> 6;0-	
Ikyl carboxylic	E ₇ (eV) Bond 2	e	0	-1.79278	e	-1,34946	0	-0.92918	o	-0.92918	-0.92918	-1.3-1946	6	81626.0	c	81626.0-	81626'0-	c	-0.9291x	81626.0-	-0,72357	81676'0-	72,427,0-	มเลอง	
parameters of a	الم (eV) Bond ا	\$10 <u>50</u> 0.	-41 92918	-0.92918	81026.0-	-0,92918	-1.79278	-1.7927R	-1,34946	-1,34946	-1.7927R	81626.0-	-0.92918	-41,92918	×10500-	81626,0-	816260-	-0 9291R	-0.92918	81626.11	816561)-	-0.9291K	17,2457	72,2457	
netrical bond	Atom	9	0	ئ	0	ن:	o	·	0	ن	٤		ئ	ئ			i	ئن	ڻ	ڻ	ئ	Ú*	ڻ	۲۰	
Table 15.101. The MO to HO intercept geometrical bond	Bond	RC (0)0-H	HC_(0) - 0H	HC,(()) - OH	(C = O(1)) (D = O(1)) (D = O(1))	RH, C, C, (O) - OH	$HC_{\mathbf{x}}(OH) = O$	$HC_{\kappa}(OH) = O$	$RC_{\mu}H_{\nu}C_{\mu}(0H) = 0$	$RC_{\mu}H_{\nu}C_{\mu}(OH) = O$	HO(O).2 H	RH.CC.(O)OH	H,C, ~ C, (0)0H	RH.C.H.C C. (0)0H	C-H (CH,	C-H (CH.)	C-H (CH) (ii)	## ## ## ## ## ## ## ## ## ## ## ## ##	H(C,C,H,C,H,-	$R - H \zeta \zeta_b(H_1 \zeta_c - R)HCH_2 - CC_c Ch$	$R - H_2C_s(R^2 - H_2C_s)C_b(R^2 - H_2C_c)CH_2 - C_2C_2C_2$	$iso(\cdot, C, (4))$ $iso(\cdot, C, (4))$ $iso(\cdot, C, (4))$	$(K^{-1}, (K^{0}))$ $(K^{-1}, (K^{0} - H_{2}C_{3})C_{3}(K^{0} - H_{2}C_{3})CH_{2} - H_{2}C_{3})CH_{2}$	$IRT(\mathcal{L}_{k}^{(i)}(H_{1}\mathcal{L}_{k}^{(i)}-R)H\mathcal{C}H_{1}-I_{1}\mathcal{C}H_{2}$	

Parallicies	() H~J	(c):2~2	Parameters $C = C(0)$ $C = C(0)$ $C = O(1)$	ن ک	0-0	HO	Œ,	Œ,	(I) H (II)	(= C (a)	(a) (b) (c) (c) (d)	(S)	(d)	(-'(e)	Group
	Group	Group	croup	dnon	droup	Grant	Group	Group	dans)	decin	design	1	<u>.</u>		
n,	-	_	23	2	-	-	3	2		-	_	-	-		-
11	0	0	0	0	0	0	2	-	0	0	0	0	0	0	0
"	0	0	0	0	0	0	0	0	0	0	0	0	0	0	٥
	0.75	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0,5
	-	-	-	-	-	-	-	1	1	_	-	1	1	1	-
	-		-	-	-	0.75		_	ı	-	-	-	1	1	1
	0.91771	17716.0	0.85395	0,85395	0,85395	-	0,91771	0.91771	0.91771	17716.0	0.91771	0.91771	17716.0	0,91771	0.91771
6.	0	0	13	2	0	-	0	-	_	0	0	0	1	1	Q
6.	-	2	4	4	2	-	-	-	i	2	2	2	2	2	2
6.	-	0	0	0	0	_		7	-	0	0	0	0	0	0
	0.75	-	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	5'0	5.0	0.5	0.5	0.5
	-	-	-	_	-	_	1	-	-	-	1	1	1	1	
J. (eV.)	-36.74167	-30.19634	-112,61934	-111.25473	-35.08488	-40.92709	-107,32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V (eV)	13.11890	9.50874	23.95107	23,87467	10,32968	14.81988	38.92728	25.78002	12.87680	9,33352	9.33352	9,37273	933352	9.37273	9.37273
/ (el/)	11,38634	7,37432	43.62389	42,82081	10,11150	16,18567	32.53914	21.06675	10.48582	6.77464	6.77464	00506'9	6.77464	6.90500	6.90500
V_ (eV)	-5.69317	-3.68716	-21.81195	-21.41040	-5.05575	-8.09284	-16.26957	-10.53337	-5.24291	3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
Elm not (cV)	-14,63489	-14.63489	0	0	-14,63489	-13,6181	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
AEusm I.m.m (eV)	-0.92918	٥	-3.58557	-2.69893	-2.69893	0	0	0	0	0	0	0	0	0	0
E, (so no) (el)	-13.70571	-14.63489	3,58557	2,69893	-11.93596	-13.6181	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-15,35946
E, [u, so] (eV)	-31,63530	-31.63534	-63.27075	-63.27074	-31.63541	-31.63247	-67.69451	-49.66493	-31,63533	-31.63537	-31.63537	-31.63535	-31,63537	-31,63535	-31.63535
E, atom - atom, msp3.AO (eV)	-	-1.85836	-3.58557	-2.69893	-1.85836	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
E, (so) (cV)	-31.63537	-33,49373	-66.85630	-65.96966	-33,49373	-31,63537	-67.69450	-49.66493	-31,63537	-33.49373	-33.49373	-33,08452	-33.49373	-33.08452	-33.08452
w (101 rad/s)	26.0575	23.3291	1856.09	59.4034	24,3637	44.1776	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E. (eV)	17.15150	15.35563	40.12366	39,10034	16,03660	29.07844	16.40846	15,97831	15.91299	6:21159	6,21159	10,19220	621159	6.29021	6.29021
E. (el.)	-0.25920	-0.25966	-0.41891	-0.40804	-0.26535	-0.33749	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
\vec{E}_{trap} (cV)	0.35532	0.10502	0.21945	0.21077	0.14010	0,46311	0.35532	0.35532 (Fa (13.458))	0.35532 (Fa (13 458))	0.12312 [2]	0.17978	0.09944	0.12312	0.12312	0.12312 [2]
Ē (eV)	-0.08153	-0.20715	-0.30918	-0.30266	-0.19530	-0.10594	-0,22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E. (eV)	0.14803	0.14803	0.11441	0.11441	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E. Gumy (el')	-31.71690	-33.70088	-67.47466	-66.57498	-33,68903	-31.74130	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33,24376	-33.59732	-33.18712	-33.18712
E (e. 10 10) (eV)	-14.63489	-14.63489	-14.63489	-14,63489	-14,63489	-13.6181	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489
Empla le, at may (el')	-(3,59844	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	٥	0	0		•
$E_n(\omega_{nr})$ (eV)	3.48357	4,43110	8.70628	7.80660	4.41925	4.41035	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Composition is given by (13.3)	Marie Marie	10 11 10	0.0	00 07-1	19 0-1	0.0	TO	111/	(LD	(ii) H.J	(-(. (3)	(F) (F)	(a) .) = .)	(1) C-C (2) C-C (3) C-C (4) C-C (4) C-C (4) C-C (5)	(e)	ر—رز روس	Ŀ	Calculated	Experimental	Relative
remnilla	Name	(i) H -)	_	0=0 (00=0	(II) (III)	֝֝֝֝֝֜֜֝֝֜֝֝֝ ֓֞֞֜֞֞֜֞֜֜֞֞֜֜֞֞֜֜֞֜֜֞֜֞֜֞֜֜֞֜֜֜֜֜֜֜֜֜֜	, n	, u			(a)				5		ą	Total Bond	Total Bond	Error
		Group	Group	Group	Group	Group	Group									į		Energy (cV)	Energy (eV)	
-		-	0	-	0	-	-	c	c	þ	-		0	0	a	0	0	21.01945	21.036	0.00079
_	Posmic acid	- 5	-	- =	: -				. =		•	c	c	0	0	0	0	33,55916	33,537	-0.00066
	Accide acid			: 0					,					-	0	0	0	45,71686	45.727	0 00022
	l'injustice actu	- 4		2 6							۰,	0	- 5	0	0	o	0	57.87456	57.883	0.00015
	Isulatine acki	2 5							۰۰ ۱		l es	•		0	c	0	0	70.03226	69.995	0.00053
	remannic actu	= 6						,	. –	-		-	0	0	0	0	0	70,10482	70.183	111000
	s-Memorinitancie acia							۱ ۳۰	. د				**	0	0	0	7	70,31679	69.989	-0.00468
	2.2-1 Amenivipropanois cero	> 0					_	ı	, -		-		. 0	0	0	0	0	82.18996	82.149	050000
	Levanore nerd	= 0		5 6				_			,-	-	-	0	0	0	0	24766	94.347	00000
_	Hephanoic actu	2 0		: 0					, «					0		0	0	106.50536	106.481	-0.00022
	Colorino acid	= 0		2 5					. ~			¢		0	0	0	0	118.66306	118,666	0 00003
٠.	Notianole acid	5 5		: :					- 20		. 00	· c	c	0	o	0	0	130,82076	130.795	07,000,0
	Compliance actu								: 5		: =			0	0	0	0	155,13616	155.176	0.00026
	Dedecanoic acid	= 4		= 4			• •		2 2	۰ د	2 2				0	0	0	179,45156	179,605	0.00085
٠.	ו בונמת בכשטוב שכום	5 5					-		! !		! ==	c		0	0	0	0	191,60926	191.606	-0.00002
Callado	rentanceaning acid	2 6				• -			2	· c	: 2			0	c	0	0	203,76696	203.948	0.00089
	rievadecanoje peld	- 4		: :			۔ ۔		2:	=	2	-	. 0	Ü	0	0	0	228.08236	228.298	0.0003
	Siezne seid	=	_	=	-	-	-	-	2	,	•	,								

		щ,												_		——- ₁				
	Exp. θ		(formic scid)		124.9 (famic acid)	106.3 (formic acid)	(26.6 (acetic soid)	110.6 (acetic acid)		IO7 (prepane)	112 (propane) 113.8 (butane) 110.8 (isobutane)	111.0 (butane) 111.4 (isobatane)	108.5 (acetone)			110.8 (isobutane)		111.4 (isobakane)	111,4 (isobutane)	
	Cal. (9)		126.88	110.76	123.44	107.71	07.521	109.63	126.03	108.44	110.49	110.49	109.30	109.44	109.44	110.67	110.76	111.27	111.27	05.701
	(o)																			
	θ _r (O																			L
	ø° €							i			15.69	69.51		70.56	70.56					72.50
nsp. AU).	E _r (eV)		c	c	-1,44915	0	-1,65376	-1,44915	-1,44915	U			0			-1.85836	0	0	-1.85836	!
tom — atom, 1	`&'		0.97600	0.0376.0	0.84115	17716.0	0.83472	0.85877	0.85257	1.15796			1.15796			0.81549	1.04887	1.04887	1.04887	
2, 15 2, (a	ຮ້		0.75	6,75	-	0.75	-	1	1	0.75			0.75			-	0.75	0.75	0.75	
were used.	J.		-	1	-	-	1	1	1	-			-			1	_	-	1	
eding angle	٣		0.75	51.0	1	0.75	1	1	1	-							0.75	0.75	0.75	
s from the prec	C ₃ Atom 2		0.85395 (Eq. (15.114))	0.85395 (Eq. (15.114))	0.86359	0.91771	0.85395 (Eq.(15.114))	0.85395 (Eq. (15.114))	0.86339	1			-			0.81549	17716.0	17710.0	17716.0	
the parameter	C ₂ Men: I		0.87495	0,87495	0.81871	-	0 81549	0.86359	0.84115	0.86359			0.86359			0,81549	0,87495	0.87495	0.87495	
e calculation of θ_r ,	Atem 2 Hybridizatien Designatien	(Table 15.3.A)	0	0	7	_	0	0	7	н			H			જ	1	pro.	1	
es [1] In th	Fredomba Mon 2		90819 21-	-13,61806	-15.75493	-14.82575	-13,61806	-13,61806	-15.75493 O _b	×			Ξ.			-16.68412 C _e	-14.82575 C _a	-14.82575 C,	-14.82575 C _e	
experimental valt	Atom 1 Hybidization Designation	(Table 15.3.A)	s	'n	អ	_	**	1	21				1			ž2	3 0	'n	'n	
lic acids and	Friendscher,		-15.55033	-15.55183 C,	-16.61853 O	5725.41-	-16,68411	-15.75493	1521.51- O	-15,75493			-15.75493			-16.68412 C.	.15.55033	-15,55033	-15.55033	
lkyl carboxy	2c' Terminal Morres (G _n)		3.8816	3.8816	13343	3.6405	4,5826	1,4944	43818	3 4252			3.4252			4.795k	4.1633	4,1633	4,7958	
meters of a	3c, Bond 3 (a,)		וננונג	2.63431	263431	1,83616	227954	163431	2.63431	211106			2.09711			1.91547	2,0323	2.09711	1,50327	
d angle para	2c' Rond 1 (a,)		2.06598	2,06598	12272.1	16431	2.86175	2,86175	227954	2,11106			2,09711			2,91547	2.91547	2,91547	2,90327	
Table 15.104. The bond angle parameters of alkyl carboxyllic acids and experimental values [1] In the calculation of θ_r , the parameters from the preceding angle were used. \mathcal{L}_r is \mathcal{L}_r (alom—alom_mpr. AlV.)	Mous of Angle		((.H (i); C = 0 (i))	(CH (D)	10°107	$\mathcal{L}(D, \mathcal{O}, \mathcal{H})$	70,5,57	0,3,37	10°00'07	H. H.	*,3°,5°,77	H°5'.37	H': JH7	77.77	H,7,72	"5°4 "5"5°5	H, 3,7)2	H, J, J, Pag.	לניניני אוני	70,0,0

CARBOXYLIC ACID ESTERS $(C_n H_{2n} O_2, n = 1, 2, 3, 4, 5...\infty)$

The alkyl carboxylic acid esters, $C_n H_{2n} O_2$, comprise a C = O functional group, and the single bond of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. Formic acid ester has a HC = O moiety that comprises a more stable C = O functional group 5 and a CH functional group. All carboxylic acid esters further comprise a COR moiety that comprises a C-O functional group and three types of O-R functional groups, one for R comprising methyl, one for R comprising an alkyl ester group of a formate, and one for R comprising an alkyl ester group of an alkyl carboxylate. The alkyl portion of the alkyl carboxylic acid ester may comprise at least two terminal methyl groups (CH₃) at each end of 10 the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, 15 isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid esters are equivalent to those in branched-chain alkanes.

The CH functional group is equivalent to that of formic acid. The alkyl carboxylic acid ester C = O and C - C(O) groups are equivalent to those given in the Carboxylic Acids section. 20 The formic acid ester C = O group is equivalent to that given in the Carboxylic Acids section except that \overline{E}_{Kvib} is that corresponding to a formic acid ester. The C - O group is equivalent to that given in the Carboxylic Acids section except that the parameters corresponding to oscillation of the bond in the transition state, \overline{E}_D (eV) and \overline{E}_{Kvib} , are those of a carboxylic acid ester. As in the case with the alkyl ethers, each O - C group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the O - C H₂-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.51) for the O - C-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO to O) = 0.85395$.

 $E_T \left(atom - atom, msp^3.AO \right)$ (Eq. (15.52)) of (1) the C = O group of alky carboxylic acid esters, (2) the C = O group of formic acid esters, (3) the alkyl carboxylic acid ester C - C(O) group, and (4) the carboxylic acid ester C - O group are equivalent to those of the corresponding carboxylic acids. The values given in the Carboxylic Acids section are -2.69893~eV, -3.58557~eV, -1.85836~eV, and -1.85836~eV, respectively. $E_T \left(atom - atom, msp^3.AO \right)$ of the C - O group matches that of the C - C(O) group. Also, as in the case of aldehydes, $C_{1o} = 2C_1$ in Eq. (15.52) for the C - C(O) group.

 $E_T \left(atom-atom, msp^3.AO \right)$ of the O-C-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is -1.13379~eV for the $O-CH_3$ group of 10 formate and alkyl carboxylates, -1.44915~eV for the O-R group of alkyl carboxylates, and -1.85836~eV for the O-R group of alkyl formates, where R is an alkyl group. Each is based on the energy match between the O AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively), the $C2sp^3$ HO of the methyl or alkyl ester group, and the carbonyl carbon. The increasing energy contributions to the single bond correspond to the increasing hybridization of linear combinations of increasing bond order. The energy contributions corresponding to one half of a double bond and those of the methyl-methyl and methylene-methylene bonds are -1.13379~eV (Eq. (14.247)), two times -0.72457~eV (Eq. (14.151)), and two times -0.92918~eV (Eq. (14.513)), respectively.

The symbols of the functional groups of alkyl carboxylic acid esters are given in Table 15.105. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid esters are given in Tables 15.106, 15.107, and 15.108, respectively. The total energy of each alkyl carboxylic acid ester given in Table 15.109 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.108 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl carboxylic acid esters determined using Eqs. (15.79-15.108) are given in Table 15.110.

Table 15.105. The symbols of functional groups of alkyl carboxylic acid esters.

Functional Group	Group Symbol
CH (formic acid ester) group	C-H (i)
C-C(O)	C-C(O)
C=O (formic acid ester)	C = O (i)
C=O (alkyl carboxylic acid ester)	C = O (ii)
(O)C-O	C-O
O-CH ₃	O-C (i)
O-R (formic acid ester)	O-C (ii)
O-R (alkyl acid ester)	O-C (iii)
OH group	OH
CH₃ group	$C-H$ $\left(CH_{_{3}}\right)$
CH₂ group	$C-H$ $\left(CH_{2}\right)$
CH (alkyl) group	C-H (ii)
CC bond (n-C)	C-C (a)
CC bond (iso-C)	$^{\circ}C-C$. (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

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2.10	o, the geome	incal bond paral	HEIGIS OF AIRYLE	ים טויה אוני אטטיה.	Table 15.100. The geometrical bond parameters of alkyl carboxylle acid esters and experimental val	cital values 1.											
Parameter	C-H (i)	C-H (i) $C-C(0)$		C=0 (ii)	0-0	0-C (i)	0 - C (ii)	0-C (iii)	$C-H(CH_3)$	$C-H(CH_i)$	C-H (ii)	C~C (a)	(9) D-D	(c) C-C	C-C (d)	(a) 2-2	C-C(I)
_	Group	Group	Group	Group	Group	Group	Group	Group		100	Group	Group	Group	Group	Group	Group	Group
٦									croup	dront	1	+	1				
	1.61341	2.04740	1.290799	1.29907	1.73490	. 1.82683	1.78255	1,80717	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2,10725
	1.03711	1,43087	1.13613	1.13977	1.31716	1.35160	1,33512	1.34431	1.04856	1.05553	1.05661	1,45744	1.45744	1.45164	1.45744	1.45164	1,45164
Bond Length 2c' (A)	1.09763	1.51437	1,20243	1.20628	1.39402	1.43047	1.41303	1.42276	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (A)	1.101 (methy) formate)	1.520 (acetic acid)	1.206 (methyl formate)	1.214 (acetic acid)	1.393 (avg. methyl formate)	1,393 (avg. methyl formate)	1.393 (avg. methyl formate)	j.393 (avg. methyl formate)	1.08 (methyl formate) 1.107 (C - H propane) 1.117 (C - H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1,122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
b,c (a,)	1,23591	1,46439	0.61267	0.62331	1.12915	1.22901	1.18107	1.20776	1.27295	1,29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
1	0.64281	0.69887	0.88018	0.87737	0.75921	0.73986	0.74900	0.74388	0.63580	0,63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

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Bond	Atom	E _T (eV) Bond I	<i>E</i> ₇ (eV) Bond 2	F _T (eV) Bond 3	E _T (eV) Bond 4	Final Total Energy C2sp [†] (eV)	(a_0)	$\binom{r_{imd}}{(a_a)}$	Economb (eV) Final	$E(C2sp^3)$ (eV) Final	, (o)	6.0	(o)	(a ₀)	(a°)
$RC_{a}(O)O-C_{b}H_{3}$	0	-0,92918	-0,56690	0	0		1,00000	0,83360	-16.32183	-	90.63	89.37	42.70	1.34246	0.00914
RC_(O)O - C_H,	ڻ	-0,56690	G	0	G	-(52.18239	17716.0	0.88392	-15.39265	-15,20178	95.01	84.99	45.76	1.27445	0,07716
HC.(O)O - C,H,C,H,R	0	-0.92918	-0.92918	0	0		1.00000	0.81549	-16.68412		93.09	16.98	43.59	1,29113	0.04399
HC.(O)O-C,H ₂ C,H ₂ R	: "	-0.92918	-0.92918	10	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	93.09	86.91	43.59	1.29113	0.04399
R'C, (0)0 - C, H, C, H, R	0	-0.92918	-0.72457	0	0		1.00000	0.82562	-16.47951		91.72	88.28	43.10	131951	0.02480
R'C_(0)0 - C,H,C,H,R (0 - C (ii))	ڻ	-0.72457	-0,92918	C	c	-153.26945	17716.0	0.82562	-16.47951	-16,28864	91.72	88.28	43.10	131951	0.02480
$HC_{a}(O) - OC_{a}H_{3}$ (C = O(1)) (O - C(1))	0	-0.92918	-0.56690	0	0		1.00000	0.83360	-16.32183		98.97	81.03	46.82	1.18716	0.13000
$ \begin{array}{l} "(O) - OC_{\mu}H_{3} \\ = O(1) \\ = O(1) \end{array} $	υ°	-0.92918	-1.79278	0	0	-154.33765	0.91771	0.77536	-17,54772	-17.35685	93.94	86.06	43.24	1.26386	0.05329
$HC_{\mu}(O) - OR$ $(C = O \ (i))$	0	-0.92918	-0.92918	0	0		000001	0.81549	-16,68412		97.48	82.52	45.73	1,21100	0.10616
HC_(O) - OR (C = O (i)) (O = C (ii))	*ن	-1.79278	-0.92918	c	0	-154.33765	17716.0	0.77536	-17.54772	-17.35685	93.94	86.06	43.24	1.26386	0.05329
$RH_2C_3C_4(0) - 0C_6H_3$ ($C = 0$ (ii) ($O - C$ (ii)	0	-0.92918	-0,56690	c	O		0.000001	0.83360	-16.32183	H ·	98.97	81.03	46.82	1.18716	0.13000
$RH_2G_2C_0(0) - 0G_0H_3$ (C = 0 (ii))		81626.0-	-1.34946	-0.92918	0	-154.82352	0.91771	0.75447	-18,03358	-17.84271	91.96	88.04	41.90	1.29138	0.02578
$RH_2C_0C_0(O) - OC_0H_2C_1H_2R$ (C = 0 (ii))	0	-0.92918	-0.72457	0	0		1.00000	0.82562	-16.47951		98.32	85.18	46.34	1.19766	0.11949
$RH_2C_n(O) - OC_nH_2C_nH_2R$ $(C = O(i))$ $(O - C (iii))$	رة	81626.0-	-1.34946	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	-17.84271	91.96	88.04	41.90	1,29138	0.02578
(OR) = O	0	-1.79278	0	0	0		1.00000	0.81871	-16,61853		137.10	42.50	65.45	0.53635	0.59978
$HC_u(OR) = O$	ئ	-1.79278	-0.92918	0	0	-154.33766	0.91771	0.77536	-17.54772	-17.35685	135,24	44,76	63.02	0.58561	0.55053
$R(C_hH_2C_u(OR) = O$ $C = O(ii)$	0	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$RC_0H_2C_a(OR) = 0$ CC = 0 (ii)	ڻ	-1.34946	-0.92918	-0.92918	0	-154.82352	0.91771	0.75447	-18,03358	-17.84272	133.47	46.53	61.46	0.62072	0.51905
H - C(O)OR	ز	-1.79278	-0.92918	0	0	-154.33766	17716.0	0.77536	-17.54772	-17,35685	69.89	11011	36.09	1.30373	0.26662
R'H ₂ C ₁ - C ₂ (0)0R	نَّ	-0.92918	-1.34946	-0.92918	0	-154.82352	0.91771	0.75447	-18,03358	-17.84272	56.25	123.75	25.37	1.85002	0.41915
H,C, - C, (O)OR	ť	-0.92918	0	o	0 ,	-152.54487	0.91771	0,86359	-15.75493	-15.56407	72.77	107.73	34.17	1.69388	0.26301
R'H,C,H,C, -C, (O)OR	ť	-0.92918	-0,92918	0	0	-153.47405	0.91771	0,81549	-16.68411	-16,49325	65.99	114,01	30.58	1.76270	0.33183
$C-H$ (CH_3)	نا	-0.92918	-	-	0	-152.54487	0,91771	0.86359	-15.75493	-15,56407	77.49	102.51	41.48	1,23504	0.18/08
C-H (CH,)	ز	-0.92918	-0,92918	0	٥	-153,47406	0.91771	0.81549	-16.68412	-16.49325	68.47	55.111	45.84	- 5480 - 5480	0.29935

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Bond	Atom	E	E	17.	E,	Final Total	,		Ermina	(Euro)	ib	в	q	*	
		(eV) Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy ('2sp³	(a ₀)	(a _n)	(eV) Final	(eV) Final	. ©	•		$\binom{a_i}{a_o}$	(a°)
(' – H (('H) (ii)	·	-0.92918	-0.92918	-0.92918	6	-154,40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_iC_iC_iH_2CH_2 - (C - C_i(a))$	ວ"	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_1C_sC_sH_2CH_2-$ ($C-C_sC_s(a)$)	ڻ'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16,49325	56.41	123.59	26.06	1.90890	0,45117
$R - H_2C_{*}C_{*}(H_2C_{*} - R)HCH_2 - (C - C^{*}(b))$	٠,٠	-0.92918	-0.92918	-0.92918	0	-154,40324	17716.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2C_a(R^a - H_2C_a)C_b(R^a - H_2C_c)CH_2 - (C - C^a, (c))$	نځ	-0.92918	-6.72457	-0.72457	-0.72457	-154,71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$IxoC_{\alpha}C_{\beta}(H_{2}C_{\beta}-R^{\alpha})HCH_{2}-(C^{\alpha}-C^{\alpha}(d))$	ر.ً	-0.92918	-0.92918	-0.92918	0	-154,40324	17716.0	0.77247	-17,61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_{\sigma}(R'-H_{2}C_{\sigma})C_{\delta}(R''-H_{2}C_{\varepsilon})CH_{2}.$ $(C-C_{\sigma}(e))$	۲.	-0.72457	-0,72457	-0.72457	-0.72457	-154.51399	0.91771	0.76763	-17.92866	-17.73779	50.04	129,96	22.66	1.94462	0.49298
$tertC_{\mu}C_{\lambda}(H_{\lambda}C_{\mu}-R)HCH_{\lambda}-(C-C^{*}(f))$	ſ.,	-0.72457	-0.92918	-0.92918	-0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$ksoC_{\mu}(R-H_2C_{\mu})C_{\mu}(R^{\mu\nu}-H_2C_{\mu})CH_2-$ (C'-C'(f))	ر.	-0.72457	-0.72457	-0,72457	-0.72457	-154.51399	17716.0	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Parameters $C-H$ (i) $C-C(O)$ $C=O$ (ii) $C=O$ (ii) Group Group Group	C-H (i) Group	C-C(O) Group	C = O(i) Group	C=0 (ii) Group	C-0 Group	O-C (i) Group	O-C (ii) Group	O-C (iii) Group	CH, Group	CH ₂ Group	C-H (ii) Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	Group Group	C-C (e) Group	C-C (f)
0 0	$n_{\rm i}$	-	_	2	2	1	1	1	-	'n	2	-	-	-	-	1	-	-
	n,	0	0	0	0	0	0	0	0	2	-	0	0	0	0	0	0	0
	H_{i}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1 1 1 1 1 1 1 1 1 1	C.	0.75	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
1 1 1 1 1 1 1 1 1 1	ڻ'	-	-	-	-	1	1	1	-		-	-	1	1	11	-	-	1
	c,	-	1	-	-	-	-	1		-	-	_	-	-	1	-	-	_
	មី	0.91771	0.91771	0.85395	0.85395	0.85395	0.85395	0.85395	0.85395	0.91771	17716.0	0.91771	0.91771	0.91771	17716.0	17716.0	17716.0	0.91771
	ن	٥	0	2	2	0	0	0	0	0	_	1	0	0	0	-	-	0
	ر.'	-	2	4	4	2	2	2	2	-	-	-	2	2	2	2	2	2
(eV) <	C,	-	0	0	0	0	0	0	0	co.	2	-	0	0	0	0	0	0
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	ر!،	0.75		0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	C ₂₀	-	-		-	-	-	1	1	_	1	_	-1	-	1	-	-	1
1311800 13.01800 13.01801 13.01801 13.01801 10.018002 10.018002 13.01801 13.01800	V, (eV)	-36.74167	-30.19634	-112.61934	-111.25473	-35.08488	-32.67173	-33.78830	-33.15757	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	V, (eV)	13,11890	9.50874	23.95107	23.87467	10.32968	10.06642	10.19070	10.12103	38.92728	25.78002	12,87680	9,33352	9.33352	9.37273	9.33352	9.37273	9.37273
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	T (eV)	11.38634	7,37432	43.62389	42,82081	10.11150	8,94219	9.47754	9.17389	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6,90500	6.90500
	$V_{m}(eV)$	-5.69317	-3.68716	-21.81195	-21.41040	-5,05575	-4.47110	-4.73877	-4.58695	-16,26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
	$E(\omega m)$ (eV)	-14.63489	-14.63489	0	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14,63489	-15,56407	-15,56407	-15.35946	-15.56407	-15.35946	-15.35946
	$\Delta E_{H,MO}(\infty no) (eV)$	-0.92918	0	-3.58557	-2.69893	-2.69893	-1.13379	-I.85836	-1.44915	0	0	0	0	0	0	0	0	0
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$E_T(so\ no)\ (eV)$	-13.70571	-14.63489	3.58557	2.69893	-11.93596	-13,50110	-12.77653	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15,56407	-15.35946	-15,35946
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$E_{\mathbf{r}}(n_2\omega)$ (eV)	-31.63530	-31.63534	-63.27075	-63.27074	-31.63541	-31,63531	-31,63536	-31.63533	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31,63535	-31.63537	-31,63535	-31,63535
(1) 31,63537 -33,49373 -68,88630 -65,89666 -33,49373 -32,78916 -33,49373 -32,78916 -33,49373 -32,78916 -33,49373 -33,69373 -33,4	$E_{\tau}(atom - atom, msp^3.AO)$ (eV)	0	-1.85836	-3.58557	-2.69893	-1.85836	-1.13379	-1.85836	-1.44915	0	٥	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
0.155 26.0575 23.3291 60.9581 59,4034 12.7206 21,4553 22.7749 12.0229 24,2786 24,2781 24,1759 9436999 943699 943699 943699 943699 943699 943699 943699 943699 943699 943699 943699 943699 943699 943699 943699 943699 943699 943699	$E_{\tau}(sw)$ (eV)	-31.63537	-33.49373	-66.85630	-65.96966	-33.49373	-32.76916	-33.49373	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
(1.15150) 15.35563 40.12366 39.10034 8.42030 14.12224 14.99083 16.0846 15.97831 15.91299 6.21159 6.21559 6.21559 6.21559	$\omega \left(10^{18} rad / s\right)$	26.0575	23.3291	1856.09	59,4034	12.7926	21.4553	22.7749	12,0329	24.9286	24.2751	24.1759	9.43699	9,43699	15.4846	9.43699	9.55643	9.55643
0.25572 0.215920 -0.215920 -0.215920 -0.215920 -0.14050 -0.19228 -0.24562 -0.25552 -0.25572 -0.22592 -0.22592 -0.16515	$E_K(aV)$	17.15150	15,35563	40.12366	39.10034	8.42030	14.12224	14.99085	7.92028	16.40846	15.97831	15.91299	6.21159	621159	10.19220	6.21159	6.29021	6.29021
0.55522 0.10502 0.21747 0.14965 0.14669 0.16188 0.35532 0.35532 0.35532 0.35532 0.15787 0.17978 0.17978 (13,458) (13,458) (12,458) (12,458) (12,458) (13,458) (14,638) (14,638) (14,638) (14,638) (14,638) (14,638) (14,638) (14,638) (14,638) (14,6348)	\vec{E}_n (eV)	-0.25920	-0.25966	-0.41891	-0.40804	-0.19228	-0.24362	-0.25655	-0.18420	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
-0.08153 -0.20715 -0.31047 -0.11745 -0.18628 -0.10361 -0.10361 -0.10360 -0.10350 -0.07200 -0.10359 -0.07256 -0.10352 -0.10362 -0.07260 -0.10359 -0.07260 -0.10359 -0.07260 -0.10359 -0.07260 -0.10359 -0.07260 -0.10359 -0.07260 -0.10359 -0.07260 -0.10359 -0.07260 -0.10359 -0.07260 -0.10359 -0.07260 -0.14803 0.1463489 0.1463489 0.1463489 0.1463489 0.1463489 0.1463489 0.1463489 0.1463489 0.1463489 0.1463489 0.1463489 0.1463489 0.1463489 0.1463489 0.1463489 0.1463489 0.1463489 0.1463489 0.1463489 0.1463489 <th< td=""><td>$ec{E}_{\mathbf{k}_{\mathbf{t},\mathbf{k}}}\left(eV ight)$</td><td>0.35532 (Eq. (13.458))</td><td>0.10502 [29]</td><td>0.21747</td><td>0.21077 [12]</td><td></td><td>0.11469 [32]</td><td>0.11469 [32]</td><td>0.16118 [4]</td><td>0.35532 (Eq. (13.458))</td><td>0.35532 (Eq. (13.458))</td><td>0.35532 (Eq.</td><td>0.12312 [2]</td><td>0.17978</td><td>0.09944</td><td>0.12312</td><td>0.12312</td><td>0.12312</td></th<>	$ec{E}_{\mathbf{k}_{\mathbf{t},\mathbf{k}}}\left(eV ight)$	0.35532 (Eq. (13.458))	0.10502 [29]	0.21747	0.21077 [12]		0.11469 [32]	0.11469 [32]	0.16118 [4]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq.	0.12312 [2]	0.17978	0.09944	0.12312	0.12312	0.12312
V) 31.71690 -33.70088 -67.47664 -65.7498 -33.6918 -33.69294 -33.1881 -67.92207 -49.8099 -31.7073 -33.59732 -33.49373 N) -31.71690 -33.70088 -67.47664 -66.57498 -33.6118 -32.95544 -33.69294 -33.18813 -67.92207 -49.80996 -31.70737 -33.59732 -33.49373 m) (eV) -14.63489<	\bar{E}_{oc} (eV)	-0.08153	-0,20715	-0.31017	-0.30266	-0.11745	-0.18628	-0.19921	-0.10361	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
-31.71690 -33.70088 -67.47664 -66.57498 -33.61118 -32.59544 -33.18813 -67.92207 -49.80996 -31.70737 -33.59732 -33.49732 <t< td=""><td>E_{mer} (eV)</td><td>0.14803</td><td>0.14803</td><td>0.11441</td><td>0.11441</td><td>0.14803</td><td>0.14803</td><td>0.14803</td><td>0.14803</td><td>0.14803</td><td>0.14803</td><td>0.14803</td><td>0.14803</td><td>0.14803</td><td>0.14803</td><td>0.14803</td><td>0.14803</td><td>0.14803</td></t<>	E_{mer} (eV)	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
-14.63489 -13.59844 0 0 0 3.48357 4.43110 8.70826 4.34141 3.68566 4.42316 3.91835 12.49186 7.83016 4.33774 4.29921	$E_{T}(\omega_{rag})$ (cV)	-31.71690	-33.70088	-67.47664	-66,57498	-33.61118	-32.95544	-33.69294	-33,18813	-67.92207	49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
-13.59844 0 0 0 0 0 -13.59844 -13.59844 -13.59844 0 0 3.48357 4.43110 8.70826 7.80660 4.4216 3.68366 4.42316 3.91835 12.49186 7.83016 3.32601 4.33754 4.29921	E untra (c. 10 110) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
3.48357 4.43110 8.70826 7.80660 4.34141 3.68566 4.42316 3.91835 12.49186 7.82016 3.32601 4.32754 4.29921	Emend (c. 10 110) (eV)	-13.59844	0	0	0	0	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
	$\vec{E}_{\mu}(\omega_{\mu})$ (eV)	3.48357	4,43110	8.70826	7.80660	4.34141	3.68566	4.42316	3.91835	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.109. The total bond energies of alkyl carboxylic acid esters calculated using the functional group composition and the energies of Table 15.108 compared to the experimental values [3]. The magnetic energy E_{rest} that is subtracted from the weighted sum of the E. Horney (2017).

*) (eV)	Relative	5	.00136	78000.	0.00005	200012	00018	.00016	00000	00000	.0000	00015	00028	.00030	.00157	(00013	651001	0000	T COOK	00087	-0.00084	00072		00034	20000	10013	20052	0.00081	
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ed sum of																												118,624	
the weight	Calculated Total Bond	Energy (e	32,71076	45.24840	93.87078	106.0369	118,1946	130.3523	154 6677	166.8254	178,9831	191.1408	203.2985	57.76366	57.63888	69.89747	81 05/70	82.23881		82.00612	87.11.28	74.18434	15702 F0	106 44313	106,26968	106.37057	118.42738	118,49994	
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Fig means where $E_{\rm log}$ that is subtracted from the weighted sum of the $E_{\rm l}$ (err) (eV)	<i>°</i> €		00		. 0	0	0 0		0	0	۰ ،	> 0	- c		, c	. 0	0	0		> 0			0	0	0	~ c		0	
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10		Methyl formate Methyl acetate			-														Ethyl pen	Ethy (3-m	Ethyl 2.2	divinciniying technicities	Propy Dentangal	Isopropy	Butyl pentanoate	sec-Buty1	Isobutyl pentanoate		
Formula	j	C,H,O,	O'H'S	5 0	CHIC	ChH ₂₀ O	OH I		CLH	ClyH ₃₀ O ₂	C ₁₆ H ₂₂ O ₂	o di	0 C	֖֓֞֞֞֓֓֓֟֓֟֓֓֓֟֓֓֓֟֓֓֓֟֓֓֓֓֟֓֓֓֟֓֓֓֟֓֓֟֓֓֓֟֓֓֓֟֓֓֓֟֓֓֓֓	֭֓֞֝֞֜֜֞֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֡֓֓֓֡֓֞֓֓֡֓֡֓֓֡֓	֓֞֝֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓		בטבוויים.	CH ₁₂ O	C,H;102	C,H,O	C.H.	0 10	C,H,O	CHIO	CHILO	OT TO		

	Exp. 6	110 fmethyl form	127 (methyl form	I 14 (methyl form	107 (propane)	112 (propane) 113.8 (butane) 110.8	(butane) 111.4	108.5	(armane)		110,8 (isobulane)		111.4 (isobutane)	111.4 (isobutane)	
	Cal. θ	109.95	127.56	114.27	108.44	110.49	110,49	109,50	109.44	109.44	110.67	110.76	111.27	111.27	1
	(0)														1
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	φ _. ©	-		-	<u> </u>	69.51	69.51		70.56	70.56					
atom, msp3.40)	E_T (eV) ·	0	-1,65376	-1.85836	0			0			-1.85836	0	0	-1.85836	
s E _r (atom –	25	0.98884	0.81710	0.78498	1.15796			1.15796			0.81549	1.04887	1.04887	1.04887	
used. E _T is	3	0.75	-	-	0.75			0.75				0.75	6.75	0.75	
s angle were	స	-	-	_	_		*	-			-	-	1	-	
e preceding	ប	0,75	-	-	-						1	0.75	0.75	0.75	
uneters from th	C ₂ Atom 2	0.85395 (Eq. (15.114))	0.81549	0.73637	1			_			0.81549	0.91771	0.91771	0.91771	
of θ_r , the para	C ₂ Aton I	0.86359	0.81871	0.83360	0.86359			0.86359			0.81549	0.87495	0.87495	0.87495	
In the calculation	Atom 2 Hybridization Designation (Table 15.3.A)	0	ß	50	н			н			æ		_	-	
il values [1].	F. Carlonthe Alon 2	-13.61806	-16.68412 O _k	-18.47690 C,	н			×			-16.68412 C _e	-14.82575 C,	-14.82575 C _o	-14.82575 C,	
rs and experiment	Atom 1 Hybridization Designation (Table 15.3.A)	7	23	91	7			7			જ	ç	'n	ŝ	
yiic acid este	E carloning Atom 1	-15.75493 C _h	-16,61853 O _a	-16.32183 C _b	-15,75493			-15.75493			-16,68412 C,	-15,55033 C,	-15.55033 C _h	-15.55033 C,	
alkyl carbox	2c'	3.9463	4,4045	4.4833	3,4252			3.4252			4.7958	4,1633	4.1633	4.7958	
rameters of	2c' Bond 2 (a _n)	2.70321	2.63431	2.63431	2.11106			2.09711			2.91547	2.11323	2.09711	2.90327	
and angle pa	2c Bond I (a ₀)	2.09711	7,27227	2.70321	2.11106			2.09711			2,91547	2.91547	2.91547	2.90327	
to the prince of any case and experimental values [1]. In the calculation of θ , the parameters from the preceding angle were used. E, is E, [atom - atom, nxp* AO]		$\angle HC_{\lambda}O_{k}$ (CH (i); $C = O$ (i))	$\angle O_{\mathcal{C}}^{\mathcal{C}}O_{\mathcal{L}}$ $(CH\ (i);\ C=O\ (i))$	$\angle C_{\nu}O_{\nu}C_{\nu}$ $(CH (i); C = O (i))$	Methylene ZHC _a H	ຳວ"ລ7	ZC,C,H	H [®] ZHZ	"כ"כ"כ	H",")"	جر 'ر' د ابه ر'	ΔC,C,H iso C,	ZC,C,H ™ C,	کرډرپرر سر ک	7C,C,C,

AMIDES
$$(C_n H_{2n+1} NO, n = 1, 2, 3, 4, 5...\infty)$$

The alkyl amides, $C_n H_{2n+1} NO$, comprise a C=O functional group, and the single bond of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. Formamide has a HC = O moiety that comprises a more stable C = O functional group and a CH functional 5 group that is equivalent to that of the CH (i) of aldehydes given in the corresponding section. It is also equivalent to that of the iso-CH group of branched-chain-alkyl portion of the alkyl amide except that E_{mog} (Eq. (15.58)) is not subtracted from $E_{D}(Group)$. All amides further comprise a $C-NH_2$ moiety that comprises a NH_2 functional group and two types of C-Nfunctional groups, one for formamide and the other for alkyl amides ($RC(O)NH_2$ where R is 10 alkyl). The alkyl portion of the alkyl amide may comprise at least two terminal methyl groups (CH₃) at each end of the chain, and may comprise methylene (CH₂), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain 15 alkanes. In addition, the C-C bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in amides are equivalent to those in branched-chain alkanes.

The NH₂ functional group was solved in the Dihydrogen Nitride (NH₂) section except 20 that the energy of the N - H MO is matched to the nitrogen-atom contribution to ΔE_{H₂MO} (AO/HO) and E_T (atom - atom, msp³.AO) of the C - N group. Both alkyl amide C = O groups and the C - C(O) group are equivalent to those given in the Carboxylic Acid Esters section except that \(\overline{E}_{Kvih}\) of the C - C(O) group is matched to that of an amide. The C - N groups are equivalent to those of alkyl amines given in the corresponding section except that the energy of the C - N group is matched to that of the C = O group and \(\overline{E}_{Kvih}\) is that of a amide. ΔE_{H₂MO} (AO/HO) of the C - N group is equal to \(\overline{E}_T\) (atom - atom, msp³.AO) of the alkyl C = O and C - N groups in order to match the energies of the corresponding MOs.

As in the case of primary amines, each C-N group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of

electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the C-N H_2 -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.52) for the C-N-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO\ to\ N) = 0.91140$.

 $E_T(atom-atom,msp^3.AO)$ (Eq. (15.52)) of the C=O group of alky amides and the C=O group of formamide are equivalent to those of the corresponding carboxylic acids and esters. The values given in the Carboxylic Acids section are -2.69893~eV and -3.58557~eV, respectively.

 $E_T \left(atom-atom, msp^3.AO \right)$ of the amide C-C(O) group is the same as alkanes, 10 aldehydes, carboxylic acids, and carboxylic acid esters, -1.85836~eV, where both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes, $C_{1o}=2C_1$ in Eq. (15.52).

In order to match energy throughout the chain of the amide molecule, $E_T(atom-atom,msp^3.AO)$ of the C-N-bond MO in Eq. (15.52) due to the charge donation 15 from the C and N atoms to the MO is -1.65376~eV. It is based on the energy match between the $C2sp^3$ HO of the carbonyl and the primary amino group NH_2 . It is given by the linear combination of -0.92918~eV (Eq. (14.513)) which matches the contiguous C-C(O) or HC(O) group and -0.72457~eV (Eq. (14.151)), the contribution of a primary amino group given in the Primary Amines section.

The symbols of the functional groups of alkyl amides are given in Table 15.111. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl amides are given in Tables 15.112, 15.113, and 15.114, respectively. The total energy of each alkyl amide given in Table 15.115 was calculated as the sum over the integer multiple of each E_D (Group) of Table 15.114 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.116.

Table 15.111. The symbols of functional groups of alkyl amides.

Functional Group	Group Symbol
CH (formamide) group	C-H (i)
C-C(O)	C-C(O)
C=O (formamide)	C = O (i)
C=O (alkyl amide)	C = O (ii)
(O)C-N (formamide)	C-N (i)
(O)C-N (alkyl amide)	C-N (ii)
NH ₂ group	$N\!H_2$
CH₃ group	$C-H$ $\left(CH_{_{3}}\right)$
CH ₂ group	$C-H$ $\left(CH_{2}\right)$
CH (alkyl) group	C-H (ii)
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Table 15.11	Table 15.112. The geometrical bond parameters of alkyl amides and experimental values [1]	כפו מסמת אמימוכני														
Parameter	C-H (i) Group	C-C(O) Group		C = O (i) $C = O$ (ii) Group Group	C – N (I) Group	C~N (ii) Group	NH ₂ Group	$C \sim H\left(CH_3\right)$ Group	$C-H\left(CH_{2}\right)$ Group	C – H (ii) Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$a(a_a)$	1.67465	2.04740	1.290799	1,29907	1.70920	1.75370	1.32297		1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	
c. (a ₀)	1.05661	1,43087	1.13613	1.13977	1,30736	1,32427	0.97065	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	L.
Bond Length 2c' (A)	1.11827	1.51437	1.20243	1.20628	1.38365	1.40155	1.02729	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	
Exp. Bond Length (A)	L.125 (formamide)	1.519 (acetamide) 1.520 (N- methylacetamide)	1.212 (formamide)	1.220 (acetamide) 1.225 (N- mchylacctamide)	1.368 (formamide)	1.380 (acetamide)	1.027 (formanide) 1.022 (acetamide)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
b,c (a_n)	1.29924	1.46439	0.61267	0.62331	1.10098	1.14968	0.89894	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
b	0,63095	0.69887	0.88018	0.87737	0.76490	0.75513	0.73369	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Dond	Atom	(eV) Bond 1	67, (eV) Bond 2	<i>E</i> ₇ (eV) Bond 3	E _T (eV) Bond 4	Final Total Energy ('2sp ³ (eV)	(a_0)	$\binom{r_{,linel}}{(a_0)}$	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	(°)	(o)	(ο) ^ζ θ	(a _n)	$\begin{pmatrix} a_2 \\ (a_0 \end{pmatrix}$
RC(O)N(H) - H C = O (i) and (ii))	2	-0 82688	0	0	0		0.93084	0.86923	-15.65263		113.90	66.10	62.13	0.61843	0.35222
$HC(O) - NH_2$ ($C = O$ ()) ($C - N$ ())	≈	-0.82688	0	0	0		0.93084	0,86923	-15.65263		103.93	76.07	50.02	1.09814	0.20922
$HC(O) - NH_2$ ($C = O$ (1) ($C - N$ (1))	ن	-0 82688	-1,79278	0	g	-(54.23535	0.91771	16627.0	-17.44541	-17 25455	18.96	83.19	44.70	1.21492	0.09244
$RH_2C_kC_k(O)-NH_2$ ($C=O$ (ii) ($C-N$ (iii)	N	-0,82688	0	0	o		0.93084	0.86923	-15.65263		100.14	79.86	48.10	1.17127	0,15300
$RH_{s}C_{s}C_{s}(O)-NH_{s}$ ($C=O$ (ii) ($C-N$ (ii)	, C,	-0.82688	-1.34946	-0.92918	0	-154.72121	0.91771	0.75878	-17.93127	-17.74041	90.51	89.49	41.30	1.31755	0.00672
$HC_{n}(NH_{2}) = 0$ $(C = O(i))$	0	-1.79278	0	0	0		1,00000	0.81871	-16.61853		137,10	42.90	65.45	0,53635	0.59978
$HC_{\nu}(NH_2) = 0$ C = O (i))	ر ً	-1.79278	0.82688	0	0	-(54.23535	12210	0,77991	-17.44541	-17.25455	135.44	44.56	63.28	0.58044	0.55569
$RC_{h}H_{2}C_{u}(NH_{2}) = O$ (C = O (ii))	0	-1,34946	0	O	0		1.00000	0.84115	-16.17521		137.27	42.73	16.31	0.52193	0.61784
$RC_hH_2C_a(NH_2) = O$ ($C = O$ (ii))	(',	-1.34946	-0.82688	-0.92918	0	-154,72121	17216.0	0.75878	-17.93127	-17,74041	133,67	46.33	61.70	0.61582	0.52395
$H-C(O)NH_2$ (CH (i))		-1.79278	-0.82688	0	0	-154,23535	0.91771	16622'0	-17.44541	-17.25455	62.39	117.61	32.13	1.41810	0.36148
$RH_2C_s-C_a(O)NH_2$	C.	-0,92918	-1.34946	-0.82688	0	-154.72121	17716.0	0.75878	-17.93127	-17.74041	57.02	122.98	25.76	1.84386	0.41299
$H_3C_b - C_a(O)NH_2$	ر*	-0.92918	0	0	0	-152.54487	17716.0	0.86359	-15.75493	-15,56407	72,27	107.73	34.17	1.69388	0.26301
$RH_2C_rH_1C_b-C_a(O)NH_2$	٠,٠	-0.92918	-0.92918	0	0	-153.47405	12210	0.81549	-16.68411	-16,49325	65.99	114,01	30.58	1.76270	0.33183
('-H (CH ₃)	C	-0,92918	0	0	0	-152,54487	17716.0	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1,23564	0.18708
$C - H$ (CH_2)	i	-0.92918	-0,92918	0	0	-153.47406	17716.0	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1,35486	0.29933
('-H (('H) (ii)	ن	-0.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_{\lambda}C_{\mu}C_{\mu}H_{\lambda}CH_{\lambda}-(C_{\mu}C_{\mu}G_{\lambda})$	౮	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	6285811	0.38106
H,Ç,Ç,H,ÇH,2— (C,—C, (a))	(ر*	-0.92918	-0.92918	O	0	-153,47406	17716.0	0,81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R - H_2C_aC_b(H_2C_c - R^*)HCH_2 - (C - C^*(b))$	C,	-0,92918	-0,92918	-0.92918	0	-154,40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2C_a(R^{*-} + H_2C_a)C_h(R^{*-} + H_2C_a)CH_2 - (C - C(C))$	ڻ	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$lsoC_{\alpha}C_{\beta}(H_{\alpha}C_{\alpha}-R^{\alpha})HCH_{\alpha}-$ (C'-C' (d))	ڻ	-0.92918	-0.92918	81626'0-	0	-154.40324	0,91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$lertC_{\omega}(R'-H_{2}C_{\omega})C_{b}(R''-H_{2}C_{\omega})CH_{2}-$ (C-C' (e))	່ວ	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	0,91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_a-R^*)HCH_2 (C-C^*(f))$	ڻ	-0.72457	-0.92918	-0.92918	å	-154,19863	0.91771	0 78155	-17,40869	-17,21783	52.78	22.721	24.04	1,92443	0,47279
isoC. (R'-H,C.)C. (R"-H,C.)CH,-	,														

Parameters $C - H(t) = C - C(t) = C - O(t)$	C-H (I)	(0)2-2	(i) O = 0	(ii) O=2	C~N (i)	C-N (ii)	NH1	CH,	CH,	C-H (ii)	C-C (a)	C-C(b)	(6) 7-7	C-C (d)	C-C (e)	C-C (A
	dionio	Croup	Cronb	Cronto	chorb	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
",	_	-	2	2	-	_	7	(C)	2			-	-	-	-	-
4	0	0	0	0	0	0	0	2	-	0	0	0	0	. 0	. -	
n_{j}	0	0	0	0	0	0		0	0	0	0	-	0		,	,
C ₁	0.75	0.5	5.0	0.5	0.5	5.0	0.75	0.75	0.75	0.75	0.5	0.5	0.5	2	2	2
C ₂		_	-	_	_		0,93613	-	-	_	-	-	3 -	3 -	3 -	C
- 61	1	_	_	_	_	-	0.75	-						- -	-	-
บ์	0.91771	0.91771	505580	0.85395	0.01140	001140	-			1	-	-	1	-	-	-
<u>c</u> ,	0	-	2	2	251	0.51140	- -	1//16.0	1//16:0	0.91771	0.9177]	0.91771	0.91771	0.91771	17716.0	0.91771
		, ,	4	7			5	0	-	-	0	0	0	-	1	0
J	_[.	7	4	4	2	2	-	-	-	-	2	2	7	2	2	2
ŭ	-	0	0	0	0	0	2	m	2	1	0	0		0	0	0
(In	0.75	-	0.5	0.5	0.5	0.5	1.5	0.75	0.75	0.75	0.5	0.5	0.5	0,5	0.5	0.5
(.) (3)	-	-	-	-	-	_	-	1	-	-	-	-	-	-	-	
V, (eV)	-35.12015	-30,19634	-112.61934	-111.25473	-38.24008	-36.88558	-78.77719	-107.32728	-70.41425	-35,12015	-28.79214	-28.79214	-29.10112	-28 79214	-29 10112	-70 101 17
V, (eV)	12.87680	9.50874	23.95107	23.87467	10.40705	10,27417	28.03446	38.92728	25.78002	12.87680	9,33352	9.33352	9 37773	0 33357	0 27772	0 27772
T (aV)	10.48582	7.37432	43.62389	42.82081	11.18655	10.51650	29.77286	32,53914	21.06675	10.48582	6 77464	6 77464	6 90500	77772	003007	600000
V, (aV)	-5.24291	-3.68716	-21.81195	-21.41040	-5.59327	-5.25825	-14.88643	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3 38737	-3.45250	3 45250
El.v 110} (eV)	-14.63489	-14.63489	0	0	-14.63489	-14.63489	-14,53414	-15.56407	-15.56407	-14.63489	-15.56407	-15 56407	-15 35946	-15 56407	15 35046	76.35046
$\Delta E_{n_1 n_2}$ (so no) (eV)	0	0	-3.58557	-2.69893	-5.23932	4.35268	-1.65376	0	0	0	0	0	0	0	0	0
$E_T(\omega no)$ (eV)	-14,63489	-14.63489	3.58557	2.69893	-9.39557	-10.28221	-12.88038	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-1535946	-15 56407	15 35046	77035 51
Ela, 10 m) (eV)	0	0	0	0	0	0	-14.53414	0	0	0	0	c		0	2	סריכוביטי
$E_T(n_2so)$ (eV)	-31.63533	-31.63534	-63.27075	-63.27074	-31,63533	-31,63537	-48.73668	-67.69451	-49,66493	-31,63533	-31.63537	-31.63537	31,63535	-31 63537	31 62525	21 63636
$E_T(atom - atom, msp^3.AO)$ (eV)	0	-1.85836	-3,58557	-2.69893	-1.65376	-1,65376	0	0	0	0	-1.85836	-1 85836	-1 44915	1 95925	1 44016	21,023,5
$E_{\tau}(uo) (eV)$	-31.63537	-33.49373	-66.85630	-65.96966	-33.28912	-33.28912	-48.73660	-67.69450	-49.66493	-31.63537	-33 49373	-33 40373	.33.08453	32 /0272	22 00469	C1644:1-
$\omega \left(10^{15} rad/s\right)$	24.1759	14.1117	60.9581	59,4034	13.0822	12.5874	59.4067	24.9286	24.2751	24.1759	9.43699	043600	15.4846	0.43600	2010000	70,000,00
$E_{K}\left(eV ight)$	15.91299	9,28860	40.12366	39.10034	8.61093	8.28526	39.10250	16,40846	15.97831	15.91299	621159	651169	10 19220	621159	10000	CHOCK.
\vec{E}_{n} (eV)	-0.24966	-0.20195	-0.41891	-0.40804	-0.19325	-0.18957	-0.39136	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	515910-	12022.0	0.15416
$\left {E_{Kvb}}(vV) \right $	0.35532 (Eq.	0.14655	0.21747	0.21077	0.17358	0.17358	0.40929	0.35532 (Eq.	0.35532 (Eq.	0,35532 (Eq.	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
(A) <u>U</u>	(15.458))					(ca)	[22]	(13.458))	(13,458))	(13.458))	[7]	[4]	[c]	[2]	[2]	[2]
E ₀₀₂ (eV)	-0.07200	-0.12867	-0.31017	-0.30266	-0.10647	-0.10278	-0.18672	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Emrg (eV)	0.14803	0.14803	0.11441	0.11441	0.14803	0,14803	0.14185	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\gamma}(\epsilon_{imag})(eV)$	-31.70737	-33.62241	-67.47664	-66.57498	-33.39559	-33.39190	-49.11003	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Eminal (c. 10.110) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,53414	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Emand le, 40 HO (eV)	-13.59844	0	0	0	0	0	-13.59844	-13,59844	-13.59844	-13.59844	0	0	0		0	0
$E_{p}(crosp)$ (cV)	3.47404	4.35263	8.70826	7.80660	4.12581	4.12212	7.37901	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.115. The total bond energies of alkyl amides calculated using the functional group

		Group	Group	Group	Group	Group	$A_{i}(I) \subset A_{i}(II) AH_{2} CH_{2} CH (II) C = C (a)$	מייים ב	(H_3)	CH,	(E)	C-C (a)	(a) こ~こ	CH (11) $C - C$ (a) $C - C$ (b) $C - C$ (c) $C - C$ (d) $C - C$ (e) $C - C$ (f)	C-C (g)	C-C (e)	C~C (B)	Calculated Total Band	Experimental Total Bond	Relative
	Tomamide	-	-	.	.	-		dinoin -										Energy (eV)		3
C-H,NO	Accianide	. 0	: -	- =	- c	- <	> -		۰ -		0 (0	0	0	0	0	0	23.68712		0.00041
	Propanamide	c								o -		٥.	۰ ،	a	0	0	0	36,15222		0.00
	Butananide	0								٠,	-	 (0 1	0	0	•	0	48,30992		-0.00
	2-Methylpropanamide	=	- =						٠, ٠	4 6	٠.	7 -	0	0	0	0	0	60.46762		9
	cntanamide								7 -	، د	۰.	0 (m.	0	0	0	0	60,51509		0000
	2-Dimethylpropananide			. c					٠,	7 (-	m (0	0	0	0	0	72.65232		000
	Hexanamide	0							n -	> -		٥.	o :	m	0	0	0	72.67890		0.000
	Detanamide	0	. –						-, -	4 V		, ,	5	0	0	0	0	84,78302		900
					-	,			-	٥	٥	9	٥	0	0	0	0	109.09842		90

Еф. в (°)		119.2 (formanide)			(formamide)	(acctamide)		122.0 (acctamide)	107 (propanc)	112 (propane) 113.8 (butane) 110.8 (isobutane)	(butanc) (butanc) 111.4 (isobutanc)	108.5 (acclane)			110.8 (isobutane)		111,4 (isobutane)	[11].4 ((sobutane)
(cal. #	108.27	118.61	119.04	116.18	124.91	116.63	124.63	121.95	108.44	110.49	110.49	109.50	109.44	109.44	110.67	110.76	111.27	111.27
3.9																		
(e)																		
, ©					_					69.51	15.60		70.56	70.56				
E ₁ (eV)	0	0	0	٥	-1.44915	-1.44915	-1.65376	-1,44915	0			0			-1,85836	0	0	-1,85836
٧٠ -	1,06823	0.98033	1.02006	0.93052	0.83596	0.88749	0.83472	0.83596	1.15796			1.15796			0.81549	1.04887	1.04887	1.04887
ن	0.75	0,75	0.75	0.75	-	-	_	-	0.75		 	0.75			-	0.75	0.75	0.75
ប៉	-	1	ı	1	-	-	1	-	-			-			1			_
ប់	-	0.75	0.75	0,75	_		1	-	-			_			1	0.75	0.75	0.75
C ₂ Atom Z		17716.0	0,93613 (Eq. (15 62))	0.85395 (Eq. (15.114))	0.83078	0.91140 (Eq. (15.116))	0.85395 (Eq. (15.114))	0.83078	-			-			0.81549	12216'0	0,91771	0.91771
€3 Atom I	0,93613 Eq. (15.62))	0.93613 (Eq. (15.62))	0.91771	0.91771	0.84115	0.86359	0.81549	0.84115	0.86359			0,86359			61218.0	0,87495	0.87495	0,87495
Atom 2 Hybridization Designation (Table 15.3 A)	H	_	z	0	17	N	0	11	Н			m			25	_	-	_
Erantombic Atom 2	=	-14.82575 C	-14.53414 N	-13,61806	-16.37720 N	-14.53414 N	-13,61806	-16.37720 N	Ξ			Æ			-16.68412	-14.82575 C,	-14.82575 C,	-14.82575
Atom I Hybridization Designation	N N	z			12	,	77.	21	7			7			55	מי		•6
L'entashe Aton 1	-14,53414	-14,53414 N	-14,82575 C.	-14.82575 C.	16,17521	-15.75493 C,	-16,68411	16.17521	-15,75493			-15,75493			-16.68412 C _k	-15.55033	-15,55033	-15,55033
2c' Terninal Atoms (a _{tt})	3,1464	3.9328	4.0825	3.7238	4.3359	4.6904	4.5607	4.312K	3,4252			3.4252			4.7958	4.1633	4,1633	4,7958
2c' !!ond 2 (a ₀)	1.94130	1,94130	2,61473	12821	2.61473	2,64855	2,27954	2,64855	2.11106			2,09711			2,91547	2,11323	2.09711	2,90327
2c' Bond I (a ₀)	1.94130	2.61473	2.11323	2.11323	2.27227	2,86175	2.86175	2.27954	2,11106			2,09711			2.91547	2.91547	2.91547	2.90327
Atoms of Angle	HNH7	$\angle C_{n}NH$ $\angle C_{n}=O\left(0\right)$	$ZHC_{\mu}N$ $ZHC_{\mu}N$ $(CH (i); C_{\mu} = O (i)$	0°,3HZ	$\angle OC_n N$ (C, = O (i))	Z(t, V, V)	0'.3'.)7	ZOC, N	Methylane /HC H	2,1',1',07	H*.5".77	Makil /HC H	3.5.37	H,7,72	Δ',C',C' iso C'.	A',C',H	H, 7, 72	70.7.77

N-ALKYL AND N,N-DIALKYL-AMIDES ($C_n H_{2n+1} NO, n = 2,3,4,5...\infty$)

The N-alkyl and N,N-dialkyl amides, $C_nH_{2n+1}NO$, comprise a C=O functional group, and the single bond of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. Formamide has a HC=O moiety that comprises a more stable C=O functional group and a 5 CH functional group that is equivalent to that of the iso-CH group of branched-chain-alkyl portion of the N-alkyl or N,N-dialkyl amide. All amides further comprise a $C-N(R_1)R_2$ moiety that comprises two types of C-N functional groups, one for formamide and the other for alkyl amides $(RC(O)N(R_1)R_2)$ where R is alkyl). The N or N,N-dialkyl moiety comprises three additional groups depending on the alkyl substitution of the nitrogen. In the case of a single methyl or alkyl substitution, the NH-C bond and NH are functional groups, and the N-C bond of a di-substituted nitrogen is the third.

The alkyl portion of the N-alkyl or N,N-dialkyl amide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. 15 The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in N-alkyl or 20 N,N-dialkyl amides are equivalent to those in branched-chain alkanes.

The NH functional group was solved in the Hydrogen Nitride (NH) section except that the energy of the N-H MO is matched to the nitrogen-atom contribution to $\Delta E_{H_2MO}(AOIHO)$ and $E_T(atom-atom, msp^3.AO)$ of the C-N group. The C-C(O) group, both N-alkyl or N,N-dialkyl amide C=O groups, and both C-N groups are equivalent to those given in the 25 Amides section.

As in the case of primary amines, each N-C group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the

N-C H_2 -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.52) for the N-C-bond MO given by Eq. (15.114) is $c_2 \left(C2sp^3HO\ to\ N\right)=0.91140$.

 $E_T(atom-atom,msp^3.AO)$ of the N-substituted amide C-C(O) group is the same as alkanes, aldehydes, carboxylic acids, carboxylic acid esters, and amides, -1.85836~eV, where both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes, $C_{1o}=2C_1$ in Eq. (15.52).

 $E_T \left(atom-atom, msp^3.AO \right)$ (Eq. (15.52)) of the C=O group of N-substituted alky amides and the C=O group of N-substituted formamide are equivalent to those of the corresponding carboxylic acids, carboxylic esters, and amides. The values given in the 10 Carboxylic Acids section are -2.69893~eV and -3.58557~eV, respectively.

 $E_T \left(atom-atom, msp^3.AO \right)$ of both C-N functional groups are the same as those of the corresponding groups of amides, -1.65376~eV. $E_T \left(atom-atom, msp^3.AO \right)$ of the singly-substituted NH-C-bond MO in Eq. (15.52) due to the charge donation from the N and C atoms to the MO is -0.92918~eV. It is equivalent to that of tertiary amines and matches the energy of the NH-C group to that of the C-N group wherein $E_T \left(atom-atom, msp^3.AO \right)$ of the latter is a linear combination of -0.92918~eV (Eq. (14.513)) and -0.72457~eV (Eq. (14.151)). $E_T \left(atom-atom, msp^3.AO \right)$ of the doubly-substituted N-C-bond MO is -0.72457~eV. It is equivalent to that of the contribution of each atom of a primary amine and also matches the energy of the N-C group to that of the C-N group by matching one of the components of $E_T \left(atom-atom, msp^3.AO \right)$ of the latter.

The symbols of the functional groups of N-alkyl and N,N-dialkyl amides are given in Table 15.117. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of N-alkyl and N,N-dialkyl amides are given in Tables 15.118, 15.119, and 15.120, respectively. The total energy of each N-alkyl or N,N-dialkyl amide given in Table 15.121 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.120 corresponding to functional-group composition of the molecule. The bond angle parameters of N-alkyl and N,N-dialkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.122.

Table 15.117. The symbols of functional groups of N-alkyl and N,N-dialkyl amides.

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Functional Group	Group Symbol
C-C(O)	C-C(O)
C=O (N-alkyl and N,N-dialkyl formamide)	C = O (i)
C=O (N-alkyl and N,N-dialkyl amide)	C = O (ii)
(O)C-N (N-alkyl and N,N-dialkyl formamide)	C-N (i)
(O)C-N (N-alkyl and N,N-dialkyl amide)	C-N (ii)
NH group	NH
N-C (N-alkyl)	N-C (i)
N-C (N,N,-dialkyl)	N-C (ii)
CH₃ group	$C-H$ $\left(CH_{_{3}}\right)$
CH₂ group	$C-H$ $\left(CH_{2}\right)$
CH (alkyl) group	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

() انا-ن	Group		2,10725	1.45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888
() () ()	Group	i	2.10725	1.45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888
C-C (g)	Group		2.12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	0.68600
(e) U-U	Group		2.10725	1.45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888
(e) (-', (e)	Group		2.12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	0.68600
(a)	Group		2.12499	1,45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	0.68600
			1.67465	1.05661	1.11827	1.122 (isobutane)	1.29924	0,63095
C-H(CH,)		Group	1.67122	1.05553	1.11713	1.107 (C-H propane) 1.117 (C-H butane)	1.29569	0,63159
C-H(CH,)		Group	1.64920	1.04856	1.10974	1.107 (C-H propane) 1.117 (C-H butane)	1,27295	0.63580
N − C (ii)	Group		1.97794	1.40639	1,48846		1.39079	0.71104
	Group		1.96313	1,40112	1,48288	I.469 (N-meth)I. avenamide)	1.37505	0.71372
HN	Group		1.28620	0.95706	1,01291		0.85927	0.74410
C-N (ii)	Group		1.75370	1.32427	1.40155	1.380 (acetamide)	1.14968	0.75513
C-N (I)	Group		1.70920	1.30736	1.38365	1.368 (formamide)	1,10098	0.76490
C=O(ii)			1.29907	1.13977	1.20628	1,225 (N-methyl- nocitamide)	0.62331	0.87737
() O=3	Group		1.290799	1,13613	1,20243	1.212 (formamide)	0.61267	0.88018
(c):2-2	Group		2.04740	1.43087	1,51437	1.520 (N-methyl- ocetomide)	1,46439	0,69837
Parameter			a (a,)	c' (a,)	Bond Length $2c'$ (A)	Exp. Bond Length (A)	h,c (a.)	
	$\frac{C-C(0)}{C-C(0)} = \frac{C-O(0)}{C-O(0)} = \frac{C-O(0)}{C-O(0)} = \frac{C-O(0)}{C-O(0)} = \frac{O-O(0)}{O-O(0)} = \frac{O-O(0)}{O-O(0)} = \frac{O-O(0)}{C-O(0)} = O-$	Parameter $C-C(O)$ $C=O$ (ii) $C=O$ (iii) $C-N$ (ii) $C-N$ (ii) NH $N-C$ (ii) $N-C$ (iii) NH $N-C$ (iii) NH $N-C$ (iii) NH $N-C$ (iii) NH $N-C$ $(iiii)$ NH $N-C$ $(iiiii)$ NH $N-C$ $(iiiiii)$ NH $N-C$ $(iiiiiii)$ NH $N-C$ $(iiiiiiii)$ NH $N-C$ $(iiiiiiiii)$ NH $N-C$ $(iiiiiiii)$ NH $N-C$ $(iiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiii$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	C-C(O) C=O (ii) C=O (iii) C-N (ii) NH N-C (ii) N-C (iii) NH N-C (iiii) C-H (CH ₂) C-H (CH ₂) C-C (iiiii) C-C (iiiiiii) C-C (iiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiii	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table 15.119. The MO to HO intercept geometrical bond parameters of N-alkyl and N,N-dialkyl amides. R,R',R" are H, methyl, or alkyl groups.	retrical bond	parameters of ì	N-alkyl and N,N	-dialkyl amides.	R, R', R" are 1	H, methyl, or all		Er is Er (atom - atom, msp3.AO)	-atom, msp³.At	6					
Bond	Atom	ائم (وV) Bond ا	Er (cV) Bond 2	F ₇ (eV) Bond 3	E ₇ (eV) Bond 4	Final Total Energy ('.2yp' (eV)	$\binom{r_{inst,el}}{(a_n)}$	(a,)	Economic (eV) Final	E(C2xp³) (eV) Final	(a)	(e)	(o)	(a,)	$\begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$
$R^{\prime}C_{\alpha}(O)N(C_{b}R) - H$ (C = O (i) and (ii) (C - N (i) and (ii)	R	-ANDERS	.n 46459	¢	o		0.93084	0.84418	-16.11722		115.47	(H.53	62.49	0.59403	0,36303
$RC_a(O)N(H) - C_aH_s$ $(C = O \ (f) \text{ and } (fi))$ $(C - V \ (f) \text{ and } (fi))$	2.	-11 8268R	-0 46459	u	0		0.93084	0.84418	-16.11722		78.61	101.39	37.00	1.56779	0.16667
$RC_n(O)N(H) - C_nH_1$ $RC_n(O)N(H) - C_nH_1$ $(C = O \ (i) \text{ and } (ii))$ $(C - N \ (i) \text{ and } (ii))$	ڻ	-0 16459	o	е	a	-152,08028	14710.0	0.88983	-15.29034	-15.09948	8337	96.63	40.00	1.50383	0.10271
$RC_{\mu}(O)(H) - C_{\mu}H_{\mu}C_{\mu}H_{\mu}$ $(C = O \ (i) \text{ and } (ii))$ $(C - N \ (i) \text{ and } (ii))$ $(N - C \ (i))$	Z.	359EN ()-	-046459	ū	9		0.93084	0.84418	-16.11722		78.61	101.39	37.00	1.56779	0.16667
$RC_a(\Omega)N(H) - C_aH_1C_aH_2R$ $(C = O \text{ (i) and (ii)}$ $(C - N \text{ (i) and (ii)})$ $(N - C \text{ (i) and (ii)}$	ڻ	-046459	81676 D-	U	0	-153.00946	17716-0	0.83885	-16.21952	-16.02866	78.02	101.39	36.64	1.57525	0.17413
$R^{\prime}C_{\alpha}(O)N(C_{\alpha}H_{\beta})-C_{\alpha}H_{\beta}$ (C=O) (f) and (fi)) (C=N) (in) and (fi))	N	-0,82688	ศฉยะบา	-0.36229	С		0.93084	0.83078	-16.37720		75.57	104.43	35.35	1,61336	0.20697
$RC_s(O)N\{C_s,H_s\}-C_bH_s$ $(C=O\ (f)\ and\ (fi))$ $(C-N\ (f)\ and\ (fi))$	υ"	45,3629	æ	c	s	-151,97798	0.91771	0.89582	-15.18804	-14.99717	82.59	97.41	39.70	1.52188	0.11549
$R^{i}C_{a}(O)N^{i}(C_{a}H_{a}C_{a}H_{a})-C_{b}H_{a}$ $(C=O\ (i)\ and\ (ii))$ $(C-N\ (i)\ and\ (ii))$ $(N-C\ (ii))$	2	11. 12648	-0.36229	-0.36229	B		0.93084	0.83078	-16,37720		75,27	104.43	35.35	1.61336	0.20697
$R^{\prime}C_{\alpha}(D)N(C_{\alpha}H_{\alpha}C_{\alpha}H_{\beta}R)-C_{\alpha}H_{\beta}$ (C=O (t) and (ii)) (C-N (t) and (ii)) (N-C (ii))	ť	-0.36229	в	Ð	5	-(5(,97798	0.91771	0.89582	-15,18804	-14.99717	82.59	97.41	39.70	1.52188	0 11549
$R^nC_n(\Omega)N'(R') - C_nH_2C_nH_2R$ $(C=O,\{0\}$ and $(ii)\}$ $(C-N,\{0\})$ and $(ii)\}$ $(N-C,\{ii)\}$	N	41,82688	-0.36229	41,36229	. 0		0.93084	0.83078	-16,37720		75.57	104.43	35.35	1.61336	0.20697
$\begin{array}{l} R^{*}C_{\mu}(O)N(R) - C_{\mu}H_{\mu}C_{\mu}H_{\nu}\\ (C=O\ (i)\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $	(ر ً	41,36229	-0.92918	0	U	-152.90716	0.91771	0.84418	-16.11722	-15.92636	7.12	102.83	36.28	1.39451	0.18812
$HC_{\nu}(0) - N(H)R$ $(C = 0 \text{ (i)})$ $(C + N \text{ (i)})$ $(C - N \text{ (i)})$ $(C - N \text{ (i)})$ $(C - N \text{ (i)})$ $(R - melny \text{ or alky})$	×	-0.82688	65431-41-	0	0		0 93084	0.84418	-16.11722	-	102.07	π.93	48.57	1,13090	0 17647
$HC_{\alpha}(O) - N(H)R$ (C = O(1)) (C - N(1)) (R - C(1)) (R - R(1)) (R - R(1))	ڻ	889ZK*0-	-1,79278	O	Ü	-154,23535	0 91771	0.77991	-17,44541	-17.25455	18.9%	83.19	.14.70	1.21492	0.09244
$HC_{\mu}(0) - V(R)R$ $(C = O \ (f))$ $(C - N \ (f))$ $(C - N \ (f))$ $(R - C \ (f))$ R = nediyl or alkyl	×	-1.82648	-0,36229	-0.36229			0.93084	0.83078	-16.37720		101.03	78.97	47.79	1.14842	0.15895
$HC_{\mu}(O) - N(R)R$ $(C = O \ (1))$ $(C - N \ (1))$ $(N - C \ (1))$	ر	-0,82688	87297.1	0	e	-154.23535	17710.0	0.77991	-17.44541	-17.25455	18.36	83.19	44.70	1.21492	0.09244

R, R' = methyl or alkyl															
$R'H_{\zeta}C_{\zeta}(O) - N(H)R$ (C = O (i)) (C - M(i)) (N - C (i)) (N - C (i))	×	-0.82688	-0,46459	e	c		0.53084	0.84418	-16.11722		98.16	P8'18	76.62	1.20446	0.11982
$RH_{\zeta}G_{\rho}C_{\rho}(O) - N(H)R$ $(C = O (ij)$ $(C - N (ij))$ $(N - C (i))$ $R = metiyd or alkyd$	ن	-0.82688	-1.34946	-0.92918	g	-154,72121	0.91771	0 73878	-17.93127	17,74041	90.31	89.49	4130	1.31755	0.00672
$R^{n}H_{c}C_{c}(0) - N(R^{n})R$ (C = O(1)) (C - N(1)) (N - C(1)) $R.R^{n} = methyl or alkyl$	~	-1),82688	-0.36229	-036229	0		0.93084	0 83078	-16,37720		97.06	82.94	45.82	1,22220	D. 10207
$K^{\prime}H_{2}G_{2}(O) - N(R^{\prime})R$ $(C = O(R))$ $(C - N(R))$ $(N - C(R))$ $R^{\prime}R = \text{incliv}f \text{ or } \text{other}f$	U U	-0 K26KK	-1.34946	-0.92918	О	-154,73121	17716.0	0.73878	-17.93127	-17.74041	15,00	89.49	41.30	1.31755	0.00672
$HC_{\alpha}(N(R^n)R) = O$ (C = O(0)) $R(R^n = H, unethyl, or alkyl)$	0	.L.79378	0	В	0		ויטאטט	0 81871	-16.61853		137.10	42.90	65.45	0,53635	0.59978
$HC_{\alpha}(W(R^{\prime})R^{\prime})=0$ (C=O(1)) R(R=H, melly), or alkylous to the control of the second of	ن	-1.79278	0.82688	с	o	-154.23535	0.91771	0 77991	-[7,4454]	-17.25455	135.44	44.36	63.28	0,58044	0.55569
$RC_{p}H_{2,n}^{-1}(V(R^{n})R) = O$ C = O (ii) $R:R^{n} = H.$ methyl, or alkyl	0	-1,34946	С	5	0		1,00000	084115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$(C_{C}, H_{1}, C_{n}, H(R^{n}), R) = O$ $(C = O(\mathbb{I}))$ $(R^{n}, R^{n} = H, methyl, or alkyl)$	ن -	-1,34946	-0.82688	-0.92918	0	-154,72121	17716.0	0 75878	-17.93127	-17 74011	133.67	46.33	61.70	0.61582	0.52395
$H - C(O)N(R^*)R^*$ $R: R^* = H$, methyl, or alkyl	·	.1.7927.к	-0.8268ж	0	0	-154,23535	17716.0	16627.0	-17.44541	-17.25455	62.39	117.61	32.13	1,41810	0.36148
$R(H_{+}, K_{-}) = C_{+}(U)/V(K^{-})/C$ $R^{+}, R^{+} = H, methyl, or alkyl$	ن	-0.92918	-13446	-0 82688	С	-154.72121	17716 0	0 75878	-17 93127	-17.74041	57.02	122.98	25.76	1.84386	0,41299
$H_3C_\mu = C_\mu(I)/V(R^*)/R^*$ $R_*R^* = H_*$ methyl, or alkyl	نٔ	-0.92918	0	0	0	-152.54487	0.91771	0 86359	-15,75493	-15.56407	72.27	107.73	74.17	1.69388	0.26301
$RH_{c}(H_{c},H_{c},H_{c},H_{c},H_{c})$ $RR_{c}(H_{c},H_{c},H_{c},H_{c},H_{c},H_{c})$	ئ	419 <u>2</u> 918	-0.9291K	0	0	-153,47405	17710.0	0.81549	-16.68411	-16 49325	(6,59	114.01	30,58	1.76270	0.33183
C-H (CH ₃)	ر	-0.92918	đ	D	=	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1,23564	0.18708
$C - H (CH_1)$	٤	-0.92918	-0.9291X	С	0	-153,47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$H_{\mathcal{L},\mathcal{L},\mathcal{H}_{\mathcal{L}}\mathcal{H}_{\mathcal{L}}}$	د ن	816260- 0.92918	916260-	-0.92918	СС	-154,40324	17719.0	0.86359	05519.71-	-17.42244	01.10	06'811	31.37	1.42988	0.37326
H,C,C,H,CH;- (('-('a))	ن	×1626.0-	x1626.0-	c	0	-153,47406	17716.0	0.81549	-16 68412	-16,49325	1178	123.59	26.06	1.90890	0.45117
$R - H_1C_sC_k(H_2C_s - R^s)HCH_1 - (C - C_1(b))$	ئ	-0.92918	-0.92918	-0 92918	0	-154,40324	17716.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_1C_s(R' - H_2C_s)C_h(R'' - H_2C_s)CH_2 - (C - C'(c))$	ئ	-0.9291R	-0.72457	-0.72457	-0.72457	-154.71860	17719,0	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$iso(\mathcal{L}_{\mathcal{L}}(H_{\mathcal{L}_{\mathcal{L}}}-H)HCH_2 - (C-C(d))$	C,	A1629.0-	4.92918	×1626'h	0	-154,40324	1,7710.0	0 77247	-17.61330	-17.42244	4830	131.70	21.90	1.97162	0.51388
$ler(C_{s}(R^{n}-H_{2}C_{s})C_{s}(R^{n}-H_{2}C_{s})CH_{2}-(C^{n}-C^{n}(e))$	ڻ:	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0 76765	-17.92866	67757.71-	30,04	129.96	22.66	1.94462	0.49298
$(C-C, (H_2C, -R')HCH_1 - (C-C, (f))$	บ	-0.72457	-0 92918	-0,92918	ċ	-134,19863	177100	0,78155	69801-71-	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$(K - H_2C_3)C_4(K^2 - H_3C_2)CH_3 - (C - C^2)C$	ڻ	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	0,91771	0.76765	-17.92866	-(7,73779	50.04	129.96	22.66	1.94462	0.49298

Table 15, 120. The energy parameters (eV) of functional groups of N-aikly and Parameters $C = C(0) = C = O(1) = C = O(1)$	C - C(O)	C = O(i)	C = O (ii)	C-N (i) C	C-N (fi)	NH	N-C (I)	N-C (ii)	CH3,	CH,	H−.7	C-C (a)	(e) J-2	(a) 2-2	() C-C	(e) ::-::::::::::::::::::::::::::::::::::	C-C (f)
	Group	Group	Group	Group	Group	Group		:	Group	Group	drost.	dages	dioio	dinin.	diodi	dinoi -	- a
""	-	2	2	-	-	-	-		3	7	-	-	-	-	-	-	-
R,	0	0	0	0	0	0	0	0	2	-	0	0	-	-	0	0	0
11.	0	0	0	0	0	0	0	0	0	. 0	0	0	0	0		٥	٥
	0.5	0.5	0.5	0.5	0.5	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0,5	0.5	25	0.5
(;	-	-	-	_	-	0.93613	-	-	-	-	ı		-	-	-	-	-
2,	-	-	-		_	0.75	-	-	-	1	1	-		-	-	-	
2,	17716.0	0.85395	0,85395	0.91140	0,91140	-	0,91140	0.91140	17716.0	0.91771	0,91771	0.91771	17716.0	0.91771	17716.0	17716.0	0.91771
	0	2	2	0	0	_	0		0	_		0	0	0	-	-	۰
6.	2	4	4	2	2		2	2	-		-	2	2	2	2	2	2
7	0	0	0	0	0	-	0	0	e.	2	-	0	0	0	0	0	٥
,	-	0.5	0.5	0.5	0.5	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
	-	-	-	-	_	-	-	-	-	_		1	1		-	-	-
1. (et.)	-30.19634	-112.61934	-111,25473	-38.24008	-36.88558	-40.92593	-31.67393	-31,36351	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29,10112	-29.10112
F (eF)	9,50874	23.95107	23.87467	10,40705	10,27417	14.21618	6.71067	9,67426	38.92728	25.78002	12,87680	9.33352	9.33352	9,37273	9.33352	9.37273	9.37273
T (eV)	7.37432	43.62389	42,82081	11.18655	10,51650	15.90963	8.06719	7.92833	32.53914	21.06675	10.48582	6.77464	6.77464	6,90500	6.77464	6.90500	6.90500
l' (el')	-3.68716	-21.81195	-21.41040	-5.59327	-5.25825	-7.95482	-4.03359	-3.96416	-16.26957	-10,53337	-5,24291	-3.38732	-3,38732	-3.45250	-3.38732	-3.45250	-3.45250
Elw nol (el')	-14.63489	0	0	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15,56407	-15,35946	-15.35946
ΔE (m) (eV)	0	-3.58557	-2.69893	-5 23932	-4,35268	-1.65376	-0.92918	-0.72457	0	0	0	0	0	0	0	0	٥
E. (no no) (eV)	-14.63489	3.58557	2,69893	-9.39557	-10,28221	-12.88038	-13.70571	-13.91032	-15.56407	-15.56407	-14.63489	-15,56407	-15.56407	-15.35946	-15,56407	-15,35946	-15,35946
E, (n, so) (eV)	-31.63534	-63.27075	-63,27074	-31.63533	-31.63537	-31.63531	-31.63537	-31.63540	-67.69451	-49.66493	-31,63533	-31.63537	-31,63537	-31,63535	-31.63537	-31.63535	-31.63535
E. (atom - atom, msp. AO) (eV)	-1.85836	-3,58557	-2,69893	-1.65376	-1.65376	0	-0.92918	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
Extraol (el')	-33.49373	-66.85630	-65,96966	-33.28912	-33.28912	-31.63537	-32,56455	-32.35994	-67.69450	-49.66493	-31,63537	-33.49373	-33,49373	-33.08452	-33.49373	-33.08452	-33.08452
w (10" rad 1.x)	14.1117	-	59.4034	13.0822	12.5874	44,9494	10,6278	10.5087	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9,55643	9.55643
E. (eV)	9,28860	40.12366	39,10034	8.61093	8.28526	29.58649	6 99543	6.91703	16.40846	15.97831	15.91299	6,21159	6.21159	10.19220	621159	6.29021	6,29021
E, (eF)	-0.20195	-0.41891	-0.40804	-0.19325	-0.18957	-0.34043	-0.17039	-0.16837	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0,20896	-0.16515	-0.16416	-0.16416
E. (el')	0.14655	0.21747 [32]	0.21077	0.17358	0.17358 [53]	0.40696	0.12944	0.12944	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13,458))	0.12312 [2]	0.17978 [4]	0.09944	0.12312 [2]	0.12312 [2]	0.12312 [2]
Ē (cF)	-0,12867	-0.31017	-0.30266	-0.10647	-0.10278	-0.13695	-0.10567	-0.10365	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E. (eV)	0.14803	0.11441	0.11441	0.14803	0.14803	0.14185	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E. (chang) (el')	-33.62241	-67.47664	-66.57498	-33.39559	-33,39190	-31,77232	-32.67022	-32.46359	-67.92207	-49.80996	-31,70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
(12) (or or, a), 3	-14,63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489
E le, o no! (cF')	0	0	0	0	٥	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
Entring (cf.)	4,35263	8,70826	7.80660	4.12581	4,12212	3.49788	3.40044	3.19381	12.49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3,62128	3.91734
Tolia (f. 12) The total hand and	of M. office	deib N N buch	ul amidec calcu	lated using the	finctional pro-	un composition	and the energi	ies of Table 15	.120 compared	to the experim	ental values [3]						
Formula Name $C-C(0)$	(0)2-2	() o=0	-3 C=3	C-N (i) C-N	HN v	N-C (i)	N-C (ii)	<i>CH</i> ₃ (CH ₂ Ch	1) U-U (1	(p) (, -(, (p)	(a) D-D	C-C (a) C-C (b) C-C (c) C-C (d) C-C (e) C-C (f)	-) (e))-	0 -		Relative
	dies		Group												(eV)	Energy	_
															1000	(CA)	000000

Atom I	2c' 2c' E Atom! E	2c' E	E. Atom I E. L.	Atom ! Economic	Ermbake		Atom 2	3	20	5	ئ	ឋ	20	ET	θ.	β	\vdash	Cal. 9	Exp. θ
Sonitz Tominos (and Atom 1 Designation Atom 2 (σ_{ρ}) Atoms (σ_{ρ}) Atoms (σ_{ρ})	Terminal terminal Alam 1 Designation Alam 2 Designation Alam 2 Designation	Alon 1 Designation Alon 2 Designation	Hybridization Alom 2 Designation	Alom 2 Designation	Hybridization Designation		Atem I		Atom 2	-	7		•	(e,)	`©	©	· ①	<u></u>	<u> </u>
:	(Table 15.3.A)	(Table 15.3.A)			(Table 15.3.A)	(Table 15.3.A)													
2.27954 2.64855 4.3243 16.17521 12 16.1722 11 0.84	4.3243 16.1722 11 12 16.1722 11 11	16.17521 12 -16.11722 · 11	12 -16.11722 11	-16.11722 · 11	ıı .		0.8	0.84115	0.84418		1	1	0.84266	-1,44915				122.51	121.8 (N-methylacetamide)
2.86175 2.64855 4.6904 -15.78493 7 -14.53414 N 0.86	4,6904 ('s, 7) 14,53414 N	-15.75493 7 -14.33414 N	7 -14.53414 N	-14.53414 N	Z		0.86	0.86359	0.91140 (Eq. (15.116))	-	1	1	0.88749	-1,44915				116,63	114.1 (N-methylacetamide)
2.86175 2.27954 4.5607 -16.68411 24 -13.61806 O 0.81549	4,5607 -16,68411 24 -13,61806 0	-16,68411 24 -13,61806 0	24 -13.61806 0	-13.61806 O	0	,	0.81	549	0.85395 (Eq. (15.114))	1	1	-	0.83472	-1,65376				124.63	
2.64855 2.80224 4.6504 C., 48 C., 14 0.73878	4,6904 -1733127 48 -16,21952 14 C.	-(7.335127 48 -(6.21952 14 C,	-1621932 14 C 14	-(6.21952 14 C. 14	14		0.75	878	0.83885	_	1		0.79881	-1.85836				118.72	119.7 (N-methylacetamide)
2.11106 2.11106 3.4252 -15.75493 7 H H 0.86359	3.4252 -15.75493 7 H H	H H H	Н Н 7	н	Н		0.86	159	_	-	1	0.75	1.15796	0				108.44	107 (propane)
			*				٠								69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
															15.69	-		110,49	111.0 (butane) 111.4 (isobutane)
2.09711 2.09711 3.4252 1.5.75493 7 H H 0.86359	3.4252 -15.75493 7 H H	-15.75493 7 H	Н Н 7	н	Н		0.863	59	1	1	1	0.75	1.15796	0				109.50	108.5 (acetone)
															70.56			109.44	
															70.56			109.44	
2.91547 2.91547 4.7958 $\frac{-16.68412}{C_b}$ 2.5 $\frac{-16.68412}{C_c}$ 2.5 0.81549	4.7958 -16.68412 25 -16.68412 25 C _c	-16,68412 25 -16,68412 25 C,	25 -16.68412 25 C _c 25	-16.68412 25 C _c 25	25		0.815	49	0.81549	-1	1	1	0.81549	-1.85836				110.67	110.8 (fsobutane)
2.91547 2.11323 4.1633 C_s 5 -14.82375 1 0.87495	4.1633 $C_{\rm c}$ 5 $C_{\rm r}$ 1	-15,55033 5 -14,82575 1 C, C, C,	5 -14.82575 I	-14.82575 I	-	1 0.874	0.874	95	0.91771	0.75	1	0.75	1.04887	0				110.76	
2.91547 2.09711 4.1633 -15.55033 5 -14.82575 1 0.87495	4,1633 -15,55033 5 -14,82575 1 C. 1	-15.55033 5 -14.82575 1 C C C C C	-14.82575 J	-14,82575	-	1 0.874	0.874	95	0.91771	0.75		0.75	1.04887	0				111.27	111.4 (isobutane)
2.90327 2.90327 4.7958 C_{F} 5 -14.82575 1 0.87495	4.7938 -15.35033 S -14.82375 T	-15.35033 5 -14.82575 I	s -14.82575 I	-14.82 <i>575</i> 1	I	1 0.87	0.87	495	17716'0	0.75	-	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
															72.50			107.50	

UREA (CH_4N_2O)

Urea, CH_4N_2O , comprises a C=O functional group and two $C-NH_2$ moieties that each comprise a NH_2 functional group and a C-N functional group. The C=O group is equivalent to that given for formamide in the Amides section except that the energy terms due to oscillation in the transition state are matched to that of urea. The NH_2 and C-N functional groups are also equivalent to those given in the Amides section. $E_T(atom-atom,msp^3.AO)$ (Eq. (15.52)) of the C=O and C-N groups are equivalent to those of formamide. The values given in the Amides section are -3.58557~eV, and -1.65376~eV, respectively.

The symbols of the functional groups of urea are given in Table 15.123. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of urea are given in Tables 15.124, 15.125, and 15.126, respectively. The total energy of urea given in Table 15.127 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.126 corresponding to functional-group composition of the molecule. The bond angle parameters of urea determined using Eqs. (15.79-15.108) are given in Table 15.128.

Table 15.123. The symbols of functional groups of urea.

Functional Group	Group Symbol
C=O (urea)	C = O
(O)C-N (urea)	C-N
NH ₂ group	$N\!H_2$

0.35222 0.20922 0.04630 0.59978 0.51559

0.61843 1.09814 1.26106 0.53635 0.62054

50.02 42.45 65.45 61.27

66.10 76.07 86.44 42.90 46.18

 $\begin{pmatrix} a_1 \\ a_0 \end{pmatrix}$

 $\begin{pmatrix} a \\ a_b \end{pmatrix}$

£ 3

(O)

WH	Group	1.32297	0.07066	0.97002	1.02729	1 027	(formamide) 1.022 (acetamide)	708080	0.0007	0,73369		
and experimental values [1]	Group	1.70920		1,30736	1.38365		1.368 (formamide)	200	1.10098	0.75480	0.707.0	
Table 15.124. The geometrical bond parameters of urea and experimental values 1.1.	C=0	1 290799		1.13613	1,20243		1.212 (formamide)		0,61267	2,333	0.88018	The same of the sa
Table 15.124, The geom	Parameter	(")"	n (n ₀)	c' (a _b)	Bond Length	(A)	Exp. Bond Length (A)		7:(%)	10-1 24	a de la companya de l	

hand reasonation from the state of the E. is E. allow - allow, my A.	matrical he	nd carameters	of urea. E. is	E_ arom - arom	.mxp'.AO						
Table 15, 125. The MO to HO intercept get.	נובנו וכשו חב	and partitioned and			-	Cinal Takel	,		Ermin	E (C2 sm 3)	- Go
Bond	Atom	E,	7,7	ri.	7.	Final total	instal	Jane	(eV)	((3)	•
		(e.V.)	(eV)	(eV)	(eV)		(a)		Final	(Aa)	>
		Bond 1	Bond 2	Bond 3	Bond 4	of Section				T HAGE	
~~~						1		20000	1,50,50,51		113,90
				•	0		0.93084	0.80923	-1.0.00.03	-	
H-NC(O)N(H)-H	z	-0.82688	0	>			0.02024	0.85923	-15,65263		103.93
		00000	~	0	-		U.S.Court				
H, NC(0) - NH,	>	-0.0700			,	100000	0 01775	0.74461	-18,27229	-18,08143	93.56
	ز	88928 0	-1.79278	-0.82688	5	1330000		-			23.767
H,NC(0) - NH;			-		•		3.00000	0.81871	-16.61853		151.10
0.000 0.000 0.000	-	-1,79278	0	9				, , , , ,	Orne or	18 081.63	133.82
1, NC, (WH2) = U		-	00000	007440	-	. (55.06223	0.91771	0.744b1	-10.41243	200101	
H NC (NH.)=0	<i>ن</i> 	-1.79278	-G.82088	00070'0"		7	-				
613/10/2/2/											

Table 15.126. The energy parameters (eV) of functional groups of urea.

Parameters	C = O	C - N	NH ₂
	Group	Group	Group
n _l	22	1	2
$n_2$	00	0	0
$n_3$	0	0	. 1
C _i	0.5	0.5	0.75
$C_2$	1	1	0.93613
P ₁	1	1	0.75
$c_2$	0.85395	0.91140	1
$c_3$	2	0	0
$c_1$	4	2	1
$c_{s}$	0	0	2
$C_{1o}$	0.5	0.5	1.5
C _{2"}	1	1	1
$V_{e}$ (eV)	-112.61934	-38.24008	-78.77719
$V_p$ (eV)	23.95107	10.40705	28.03446
T(eV)	43.62389	11.18655	29.77286
$V_m$ (eV)	-21.81195	-5.59327	-14.88643
E(лотно) (eV)	0	-14.63489	-14.53414
$\Delta E_{H_2MO}(AOIHO)$ (eV)	-3.58557	-5.23932	-1.65376
$E_T(MOIHO)$ (eV)	3.58557	-9.39557	-12.88038
E(n, AOIHO) (eV)	0	0	-14.53414
$E_T(H_2MO)$ (eV)	-63.27075	-31.63533	-48.73668
$E_r(atom-atom, msp^3.AO)$ (eV)	-3.58557	-1.65376	0
$E_{T}(MO)$ (eV)	-66.85630	-33.28912	-48.73660
$\omega \left(10^{15}  rad  /  s\right)$	19.9334	13.0822	59.4067
$E_{\kappa}$ (eV)	13.12053	8.61093	39.10250
$\overline{E}_{p}$ (eV)	-0.23955	-0.19325	-0.39136
$ar{E}_{K\!v\!ib}$ (eV)	0.21747 [32]	0.17358 [33]	0.40929 [22]
$\overline{E}_{asc}$ $(eV)$	-0.13081	-0.10647	-0.18672
$E_{\text{mag}}(eV)$	0.11441	0.14803	0.14185
$E_r(Grup)$ (eV)	-67.11793	-33.39559	-49.11003
$E_{initial}(c_{\star}$ логно) (eV)	-14.63489	-14.63489	-14.53414
$E_{imbol}(c_s AOIHO) (eV)$	0	0	-13.59844
$E_{\Omega}(Group)$ (eV)	8.34955	4.12581	7.37901

Table 15.127. The total bond energies of urea calculated using the functional group composition and the energies of Table 15.126 compared to the experimental values [3].

10.120 0011	pared to the experimental var	<u> </u>					
Formula	Name	C = O	C-N	$NH_2$	Calculated Total Bond	Experimental Total Bond	Relative Error
		Group	Group	Groun	i otai Bond	i otat Bond	
				Group	Energy (eV)	Energy (eV)	
CH₄N ₂ O	Urea	1	2	2	31.35919	31.393	0.00108

Table 15.128. The bond angle parameters of urea and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(anom-anom,msp^2,AO)$ .

			~		_		_	
	Exp. θ (°)				119.2	(formamide)	125.0	
	Cal. θ (°)		1	108.27	17971	10.01	1	-
	(6)							•
	9.0							•
	φ [*] (o)							
	E _T (eV)		•	>	o		21.0441.2	
.(00:	20'		0.75 1 06823		0.98033		205280	2000
4	ช		0.75		0.75			
	ů.				_		-	
-	ن ت		-		0.75		-	
( OV: downtyman 12 - 1	C ₂ Atom 2		_		0.91771		0.83078	
	C ₂ Atom I	0.02612	U.25013	(10)(10)	0.93613 (Fo (15.62))	11	0.84115.	
	Atom 2 Hybridization Designation (Table 15.3.A)		ĸ		-		11	
	E coetourbee Atom 2		Ξ	-14.82575	ز	AC777 A1-	2	
	Atom I Hybridization Designation (Table 15.3.A)		z		z		[2	
	Frankashe Atom I		-14.53414	11 53414	N	16.17521	0	
	2c' Tenninal Atons (up)	1711	3,1404		3,9328		4,3359	
	2c' Ibmd 2 (a ₆ )	101120	1,54130		1.94130		2.01473	
	2c.  Bond 1 (a _n )	1 05/130	1.54151		5/t-14/2	2 27227	777177	
Alone of Angle		HNH	Time!	77. NE	Z, "M7	N .X//	**************************************	

CARBOXYLIC ACID HALIDES (
$$C_n H_{2n-1}OX$$
,  $X = F, Cl, Br, I$ ;  $n = 1, 2, 3, 4, 5...\infty$ )

The alkyl carboxylic acid halides,  $C_nH_{2n-1}OX$ , comprise a C=O functional group, and the single bond of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. All carboxylic acid halides further comprise a C-X functional group where X is a halogen atom. The alkyl portion of the alkyl carboxylic acid halide may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid halide C=O and C-C(O) groups are equivalent to those 15 given in the Aldehydes section and the Ketones section, respectively. The values of  $E_T \left(atom-atom,msp^3.AO\right)$  given in these sections are -2.69893~eV and -1.44915~eV, respectively.

As in the case of alkyl halides, each (O)C - X group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the X AO to form a MO permits each participating orbital to decrease in radius and energy. For example, to meet the equipotential condition of the union of the (O)C - Cl  $H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $C_2$  of Eq. (15.52) for the (O)C - Cl-bond MO given by Eq. (15.111) is  $C_2(C2sp^3HO\ to\ Cl) = 0.81317$ . The solution is equivalent to that of the alkyl chloride bond except that the energy parameters corresponding to oscillation in the transition state are matched to those of a carboxylic acid chloride.

As in the case with the C-Cl group of alkyl chlorides,  $E_T(atom-atom, msp^3.AO)$  of the (O)C-Cl-bond MO in Eq. (15.52) of alky carboxylic acid chlorides due to the charge donation from the C and Cl atoms to the MO is  $-1.44915 \, eV$  where both energy contributions

are given by Eq. (14.511). This matches the energy of the C - C(O) functional group with that of the (O)C - Cl group within the carboxylic acid chloride molecule.

The symbols of the functional groups of alkyl carboxylic acid chlorides are given in Table 15.129. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), 5 and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid chlorides are given in Tables 15.130, 15.131, and 15.132, respectively. The total energy of each alkyl carboxylic acid chloride given in Table 15.133 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.132 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid chlorides determined using Eqs. 10 (15.79-15.108) are given in Table 15.134.

Table 15.129. The symbols of functional groups of alkyl carboxylic acid chlorides. Functional Group Symbol C-C(O) C = 0 (alkyl carboxylic acid chloride) C = 0 (O)C-CI

C=0 C-Cl C-H (CH₃) C-H (CH₃) C-H (CH₃) C-C (a) C-C (b) C-C (b) C-C (c) C-C (d) C-C (d) C-C (d)

CH, group
CH (alkyl) group
CC bond (n-C)
CC bond (ser-C)
CC (iso to iso-C)
CC (ito t-C)
CC (tto t-C)

CH, group

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Table (5,130. The geometrical bond parameters of alkyl carboxylic acid cilotidical parameter $C - C(O)$ $C = O$ $C - CI$ $C - CI$	<u>5</u> ]	C-Cl	$C - H(CH_3)$	C-H (CH ₂ )	C-H Group	C-C(a) Group	C~C(b) Group	رم (د) Group	Group	Group	Group
Group		Group	Group	Group		00707	117400	2 10725	2.12499	2,10725	2,10725
1 20007		2 32621	1,64920	1.67122	1.67465	7.12499	4,12477	4.1012		17.55	1 45154
10000		76102	1,04956	1 05553	1.05661	1,45744	1.45744	1.45164	1.45744	1.45164	+010+.1
1.13977		1.691.50	0.040.1	200001							
1.20628		1.79005	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1,53635
							200	1 527	1 532	1,532	1.532
1.187			1,107	1.107 (C - H monane)		1.532 (propane)	(propane)	(propane)	(propane)	(propane)	(propane)
(acetyl chloride)		1.798	(C-n propanc)	(c) (c 11)	(isobutane)	1.531	1.531	1.531	[53]	1,551	(hutane)
1.214		(acetyl chloride)	1.117	(T. H. Sutane)		(butane)	(butane)	(butane)	(butane)	(Odlanic)	Commo .
(acetic acid)			10-7 utilalic	Common Common	1 JOHN 1	1 54616	1.54616	1.52750	1.54616	1.52750	05/25.1
0.62331		1,59705	1,27295	69067'1	+76671	21010.1	00,000	0.60908	0.68600	0.68888	0,68888
			00357	0,63150	560590	0.68600	0.68600	0.0000	0.0000		

**WO 2**007/051078

wo	20	07/	/05	<b>51</b> 0	78								6	50			
$\begin{pmatrix} d_2 \\ (a_0 \end{pmatrix}$	0.30463	0.44625	0.61784	0.53901	0.39408	0.24675	0.18708	0.29933	0.37326	90186.0	0.45117	0.51388	0.50570	0.51388	0.49298	0.47279	0.49298
$\begin{pmatrix} d_1 \\ (u_0) \end{pmatrix}$	1.99599	2,13760	0.52193	9.60076	1.82495	1.67762	1.23564	1.35486	1.42988	1.83879	06806'1	1.97162	1.95734	1,97162	1.94462	1,92443	1.94462
(°)	30.90	23.23	66,31	62.45	26.96	34,98	41.48	35.84	31,37	30.08	26.06	21.90	21.74	21.90	22.66	24.04	22.66
(°)	110.38	125.31	42.73	45.72	120.70	106.38	102.51	111.53	118.90	116.18	123.59	131.70	131.79	131.70	129.96	127.22	129.96
. <del>(</del> 6)	69.62	54.69	137.27	134,28	59.30	73.62	77.49	68.47	61.10	63.82	56.41	48.30	48.21	48.30	50.04	52.78	50.04
$E(C2sp^3)$ (eV) Final		-17.43350		-17.43350	-17.43350	-15.35946	-15.56407	-16.49325	-17.42244	-15.56407	-16.49325	-17.42244	-17.73779	-17.42244	-17.73779	-17.21783	-17.73779
$E_{contourb}$ (eV) Final	-15.55033	-17.62436	-16.1752i	-17,62436	-17.62436	-15.55033	-15.75493	-16.68412	-17,61330	-15.75493	-16.68412	-17.61330	-17.92866	-17,61330	-17.92866	-17.40869	-17,92866
$(a_0)$	0.87495	0.77199	0.84115	0.77199	0.77199	0.87495	0.86359	0.81549	0.77247	0.86359	0.81549	0.77247	0.75889	0.77247	0.76765	0.78155	0.76765
$\begin{pmatrix} I'_{aitral} \\ G_0 \end{pmatrix}$	1.05158	17716.0	1.00000	17716.0	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	17710.0	0.91771	0.91771	0.91771	0.91771	0.91771
Final Total Energy C2sp³ (eV)		-154.41430		-154,41430	-154.41430	-152.34026	-152.54487	-153.47406	-154.40324	-152.54487	-153.47406	-154.40324	-154.71860	-154.40324	-154.51399	-154.19863	-154,51399
$E_{r}$ (eV) Bond 4	0	0	0	0	0	0	0	0	0	0	0	0	-0.72457	0	-0.72457	-0	-0.72457
E _r (eV) Bond 3	0	-0.72457	0	-0.72457	-0.72457	0	0	0	-0.92918	0	0	-0.92918	-0.72457	-0.92918	-0.72457	-0.92918	-0.72457
(eV) Bond 2	0	-0.72457	0	-0.72457	-1,34946	0	0	-0.92918	-0.92918	0	-0.92918	-0.92918	-0.72457	-0 92918	-0.72457	-0.92918	-0.72457
(eV) Bond 1	-0.72457	-1,34946	-1.34946	-1.34946	-0.72457	-0.72457	-0.92918	-0.92918	-0.92918	-0.92918	-0 92918	-0.92918	-0 92918	-0 92918	-0.72457	-0.72457	-0.72457
Atom	2	ن ا	0	ن'	ئن	ئ	i	Ü	ن	ບ້	ئ	υ ⁴	ť	٠ -	ڻ	ť	υ [*]
Bond	H.C.C (0)-CI	H,C,C, (0)-Cl	H,C,C,C,C)=0	$H_1C_nC_n(CI) = 0$	$H_3C_b-C_a(O)-Cl$	$H_3C_b - C_a(O) - Cl$	$C-H(CH_3)$	$C-H\left(CH_{2}\right)$	$C-H\left(CH\right)$ (ii)	$H_3C_C, C_1, H_2CH_2$	$H_3(C_1, H_2(H_2 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H_3 - H_3(H$	$R - H_2^{C}(C_k(H_2^{C} - R)HCH_2 - CC_2(B))$	$R - H_2C_a(R - H_2C_a)C_b(R^{n} - H_2C_c)CH_2 - CC_c(C_0)$	$iso(C_aC_b(H_2C_c-R)HCH_2-(C_aC_b))$	$tertC_{*}(R-H_{1}C_{d})C_{s}(R^{*}-H_{2}C_{c})CH_{2}-C_{c}(C-C^{*}(e))$	$len(C_{i}(H_{1}C_{i}-R)HCH_{1}-G_{1}C_{2}-R)HCH_{2}-G_{2}G_{2}G_{3}G_{3}G_{4}G_{4}G_{4}G_{4}G_{5}G_{5}G_{5}G_{5}G_{5}G_{5}G_{5}G_{5$	$isoC_u(R^1 - H_2C_d)C_h(R^n - H_2C_c)CH_2 - (C - C^2(f))$

Table 15.131. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid chlorides.  $R_iR_i$  are H or alkyl groups.  $E_r$  is  $E_T(arom-atom,mxp^3.AO)$ .

-	(0,0)	,	7			V::/ H - U	(6)	(A) (F)	(3) .) = .)	でして	رق ن کن	€ 1
Group Group Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
n,	-	2	_	3	2		-	<b>,</b>	-	1	1	-
n,	0	0	0	2	-	0	0	0	0	0	0	0
n,	0	0	0	0	0	0	0	0	0	0	0	0
	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	5,0	5.0	0.5
C	1	_	0.81317	_	-	_	1	1		1	1	1
2, 2	_	1	-	_		-	-	-	1	1	1	1
้	0.91771	0.85395	-	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
2,	0	2	-	0	-		0	0	0		-	0
· · ·	2	4	2	-	-	1	2	2	2	7	2	2
7 3	0	0	0	3	2	-	0	0	0	0	0	0
	-	0.5	0.5	0.75	0.75	0.75	0.5	6,0	0.5	6.5	6.5	0.5
	_	1	0.81317		-		ı	1	1	1	-	-
V, (eV)	-30.19634	-111.25473	-29.68411	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V (eV)	9,50874	23.87467	8.04432	38.92728	25.78002	12.87680	9,33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	7,37432	42.82081	6.38036	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V. (cV)	-3.68716	-21.41040	-3.19018	-16.26957	-10.53337	-5.24291	-3,38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(10 100) (eV)	-14.63489	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15,35946	-15.35946
ΔΕ _{π,30} (30 10) (eV)	0	-2.69893	-1.44915	0	0	0	0	0	0	0	0	0
E, (40 110) (eV)	-14.63489	2.69893	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
$E_{r}(u, w) (eV)$	-31.63534	-63.27074	-31,63536	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31,63535	-31.63537	-31.63535	-31.63535
$E_r(atom - atom, msp^3.AO)$ (eV)	-1.44915	-2.69893	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
E. (sw) (cV)	-33.08452	-65.96966	-33,08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33,08452	-33.49373	-33.08452	-33.08452
@ (1013 rad/s)	16,4962	59.4034	7.42995	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_{\rm r}$ (eV)	10,85807	39.10034	4.89052	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6,21159	6.29021	6.29021
E., (eV)	-0.21568	-0.40804	-0.14475	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Exis (eV)	0.14655	0.21077	0.09063	0.35532 (Fq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312 [2]
$\overline{\mathcal{E}}_{-}$ (eV)	-0.14240	-0.30266	-0.09943	-0.22757	-0,14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Emme (eV)	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E. (imm) (eV).	-33,22692	-66.57498	-33,18395	-67.92207	-49.80996	-31.70737	-33,59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Estimate, 30 110) (eV)	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Enited le. 10 10) (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
E. Grand (eV)	3.95714	7.80660	3.76614	12,49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

C-C (f)

Table 15.133. The total bond energies of alkyl carboxylic acid chlorides calculated using the functional group composition and the energies of Table 15.102 compared to the experimental values [3].

Formula Name C - C(O) C = O C - CI CH, CH, CH, C - C (a) C - C (b) C - C (c) C - C (d) C - C (e) C - C (e) C:H:CIO Acetyl chloride

110.8 (isobutane) 111.4 (isobutane) | 111.6 | (acary) (acary) (acary) (acary) (acary) (acary) (acary) (abloride) | (acary) (abloride) | (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (acary) (a 111.4 (isobutane) Exp. θ 109.44 107.50 (al. *b* 125,70 110,98 110.67 110.76 111,27 111,27 ور ت 9 0 70.56 72.50 69.51 69.51 ø* © -1.65376 -1.85836 -1.85836 -0.92918 -0.92918 Ε_τ (eV) 0 0 0 0.83472 0.84522 1.15796 1.15796 1,04887 1.04887 1.04887 Table 15.134. The bond angle parameters of alkyl carboxylic acid chlorides and experimental values [1]. In the calculation of  $\theta_{\omega}$ , the parameters from the preceding angle were used. 0.75 0.75 0.75 0.75 0.75 0.81317 (Eq. (15.111)) 0.81317 (Eq. (15.111)) ٣ ڻ 0.75 0.75 0.75 0.85395 (Eq. (15.113)) 0,87495 0.81549 17716.0 0.91771 C₂ Afom 2 0.81549 0.86359 0.86359 0.87495 0.87495 0.86359  $c_{\rm 2}$ (Table 15.3.A) ರ S 52 I Ξ -16.68412 *C*, -14.82575 C, -14.82575 C, -14.82575 C_c -12.96764 (7 -15,55033 Atom f Hybridization Designation (Table 15.3.A) 73 52 22 -16.68412 O -16.68412 *C*, -15.75493 (', -15,75493 -15.55033 C_a -15.55033 C, -15.55033 C_k E Contombie Atom l -16.68411 -15.75493 2c' Teminal Alours (a_n) 4.5826 3,4252 3,4252 4.1633 4.9841 4.1633 4.7958 5.1539 4.7958 2,11106 2.0971 2.09711 2.91547 2.11323 2.90327  $\frac{2c}{\mathrm{Band}}$ 2,27954 3,38271 2.86175 2.11106 2.09711 2,90327  $2c^{i}$ Bond 1  $(a_{0})$ 2.27954 ZC"C,"C  $\frac{ZC_aC_bC_c}{ZC_aC_bH}$   $\frac{ZC_bC_aC_c}{ZC_bC_aC_c}$ iso  $C_a$   $\frac{150 C_a}{150 C_a}$ 1.1"..." W;307  $\angle C_aC_bH$ 2C, C, H iso C, 2C, C, C, C, tert C, ΔC, C, C, C, Methylene ZHC, H Methyl ZHC "H

 $E_r$  is  $E_r$  (atom – atom, msp³.AO)

### CARBOXYLIC ACID ANHYDRIDES ( $C_n H_{2n-2} O_3$ , $n = 2,3,4,5...\infty$ )

The alkyl carboxylic acid anhydrides,  $C_nH_{2n-2}O_3$ , have two (O)C-O moieties that each comprise C=O and C-O functional groups. The single bond of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. The alkyl portion of the alkyl carboxylic 5 acid anhydride may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid anhydrides are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid anhydride C = O and C - C(O) groups are equivalent to those given in the Carboxylic Acid Esters section and the Ketones section, respectively. The values of  $E_T(atom-atom,msp^3.AO)$  given in these sections are -2.69893~eV and -1.44915~eV, respectively. The C-O group is also equivalent to that given in the Carboxylic Acid Esters section except that  $E_T(atom-atom,msp^3.AO)$  is equivalent to that of an alkyl ether as given in the corresponding section and the energy terms due to oscillation in the transition state are matched to that of a carboxylic acid anhydride.

For the C-O group,  $E_T(atom-atom,msp^3.AO)$  is  $-1.65376\ eV$ . It is based on the energy match between the O AO and the  $C2sp^3$  HO of each C-C(O) group and is given by the linear combination of  $-0.72457\ eV$  (Eq. (14.151)) and  $-0.92918\ eV$  (Eq. (14.513)), respectively. This matches  $-0.72457\ eV$ , the energy contribution of each of the  $C2sp^3$  HOs to each C-C(O) functional group, with that of the corresponding energy component of the C-O group and gives a minimum energy within the carboxylic acid anhydride molecule.

The symbols of the functional groups of alkyl carboxylic acid anhydrides are given in Table 15.135. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid anhydrides are given in Tables 15.136, 15.137, and 15.138, respectively. The total energy of each alkyl

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carboxylic acid anhydride given in Table 15.139 was calculated as the sum over the integer multiple of each  $E_{D}(G_{roup})$  of Table 15.138 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid anhydrides determined using Eqs. (15.79-15.108) are given in Table 15.140.

Table 15.135. The symbols of functional groups of alkyl carboxylic acid anitydrides.	Group Symbol	(0)2~2	ide) C=0	0-0	$C \rightarrow H \left( CH_3 \right)$	('-H)	H)	(,-(, (a)	(p) .)	ر، ۱۰ (۵)	(p)	(e) .)	
Table 15.135. The symbols of fun	Functional Group	C-C(0)	C=O (alkyl carboxylic acid anhydride)	0-0(0)	CH, group	CH; group	CH (alkyl) group	CC bond (n-C)	CC bond (iso-C)	CC bond (tert-C)	CC (iso to iso-C)	CC (t to t-C)	

Table 15,136	Table 15.136. The geometrical bond parameters of alkyl carbon	and parameters of alk	yl carboxylic acid a	xylic acid anhydrides and experimental values [1	mental values [1].							
Parameter	dno.15 ( <i>O</i> ).22	C=0 Group	Group	$C = H \left( CH_3 \right)$ Group	$C - H\left(CH_2\right)$ Group	Group Group	C~C (a) Group	Group Group	C~C (c) Group	ر–ر (q) Group	C-C (e) Group	C-C (f) Group
$\sigma\left(a_{n}\right)$	2.04740	1.29907	1.73490	1.64920	1.67122	1.67465	2,12499	2.12499	2.10725	2,12499	2,10725	2.10725
$c'(a_0)$	1.43087	1.13977	91/15.1	1,04856	1,05553	1.05661	1,45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2c' (A)	1.5143.7	1.20628	1.39402	1.10974	1,11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1,53635
Exp. Bond	1.520	,	1393	1.107			1.532	1.532	1.532	1.532	1.532	1,532
Length	(acetone)	1.214 (acetic acid)	(avg. methyl	(C - H propane)	(C - H propane)	f.122 (fenhutane)	(propane)	(propane)	(propane)	(propane)	(propane)	(propane)
(4)	(2-butanone)	,	formate)	(C-H butane)		(maccana)	(butane)	(butane)	(butane)	(butane)	(butane)	(butane)
$b,c$ $(a_n)$	1,46439	0.62331	1.12915	1,27295	1,29569	1,29924	1.54616	1.54616	1,52750	1.54616	1.52750	1,52750
v	0.69887	0.87737	0.75921	0.63580	0.63159	0.63095	0.68600	0.68600	0,68888	0.68600	0.68888	0.68888

Table 15.137. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid anhydrides. R,R',R" are H or alkyl groups.	netrical bon	d parameters of	'alkyl carboxylic	acid anhydrides	. R, R', R" are	H or alkyl grou		$E_r$ is $E_r(atom - atom, msp^3.AO)$	$r_{5}p^{3}.AO$ .						
Bond	Atom	E.	E.	E	E	Final Total		r _{fen}	Eroutomb	$E(C2sp^3)$	θ.	- l ₀	θ	ď	ď
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C2 $\eta^{j}$ (eV)	(a)	(a _e )	(eV) Final	(eV) Final	<u></u>	(6)	(0)	$(a_o)$	(ao)
RC,H,C,(0)-0,-C,(0)C,H,R'	0	-0.82688	-0.82688	c	0		1,00000	0.82562	-16.47951		98.32	87.68	46.34	1.19766	0.11949
$RC_{\mu}H_{\nu}C_{\mu}(O)-O_{\mu}-C_{\mu}(O)C_{\nu}H_{\nu}R^{\nu}$	ا ان	-0.82688	-1,34946	-0.82688	0	-154.51660	17716.0	0.76753	-17.72667	-17,53580	93.21	86.79	42.74	127417	0.04298
$RC_{r}H_{2}(R^{r}C_{r}H_{2}C_{s}(O_{s})O)C_{s}=O_{s}$	o°	-1.34946		0	0		1,00000	0.84115	-16.17521		137.27	42.73	66,31	0.52193	0.61784
$RC_{\mu}H_{2}(R^{*}C_{\mu}H_{2}C_{\mu}(O_{\mu})O)C_{\mu}=O_{\mu}$	ن	-1.34946	-0.72457	-0.82688	0	-154.51660	17716.0	0.76753	-17.72667	-17.53580	134,08	45.92	62.20	0,60583	0.53394
$RH_2C_b - C_a(O)OC_a(O)C_cH_2R'$	ئ	-0.72457	-1,34946	-0,82688	0	154,51660	0.91771	0.76753	-17.72667	-17,53580	58.55	121.45	26,56	1.83133	0.40045
$H_3C_k - C_a(O)OC_a(O)C_cH_2R'$	C.*	-0.72457	0	G	0	-152,34026	0.91771	0.87495	-15.55033	-15.35946	73.62	106.38	34,98	1.67762	0.24675
$RH_2C_b - C_a(O)OC_a(O)C_aH_2R'$ $R = alkvl$	ಭ	-0.72457	-4,92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28865	67.40	112.60	31.36	1.74821	0.31734
$C - H$ $(CH_3)$	i	40,92918	0	0	0	-152.54487	. 17716.0	0,86359	-15.75493	-15.56407	77.49	102,51	41.48	1.23564	0.18708
$(C-H(CH_2))$	j	-0.92918	-0,92918		0	-153.47406	0,91771	0.81549	-16,68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C - H\left(CH\right)$ (ii)	١	-0,92918	-0,92918	-0.92988	0	-154.40324	0.91771	0.77247	-17.61330	-17,42244	61.10	118.90	31.37	1.42988	0.37326
$H_3^{\zeta}C_p^{\zeta}H_2^{\zeta}H_2^{\zeta}-$	Ü	-0.92918	c	0	0	-152.54487	0.91771	0.86359	-15.73493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3^{(1)}(C, H_3^{(2)}(H_3 - C))$	ť.;	-0,92918	-0.92918	Б	-0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R - H_{\mathcal{L}}(L_{\delta}(H_{\mathcal{L}}^{C} - R))HCH_{\delta} - CC - C(B)$	ن	-0.92918	-0.92918	-0.92918	0	-154.40324	0 91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$(R - H_2C_a)C_b(R^a - H_2C_a)C_b(R^a - H_2C_b)CH_2 - (C - C C_b)$	ر. ا	-0.92918	-0,72457	-10,72457	-0.72457	-154,71860	17716.0	0.75889	-17.92866	-(7,73779	48.21	[31.79	21.74	L.95734	0.50570
$isoC_{c}(\cdot,\{H_{2}C_{c}-R^{\prime}\}HCH_{2}-R^{\prime}\}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime}HCH_{2}-R^{\prime$	رځ	-0.92918	-0.92918	-0.92918	0	-154,40324	0,91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$(R - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}(R^2 - R_2^{-1})^{C_3}$	ئ .	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	17716.0	0.76763	-17.92866	97757.71-	50.04	129.96	22.66	1.94462	0.49298
$\operatorname{tert}(\mathcal{L}_{\mathcal{L}}^{L}(H_{\mathcal{L}}^{L}, -R))H(H_{\mathcal{L}}^{L} - R)$	:5	-0.72457	-0.92918	-0.92918	÷	-154,19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0,47279
$soc_{a}(R-H_{2}C_{a})C_{b}(R^{a}-H_{2}C_{c})CH_{2}-C_{c}CH_{2}C_{c}$	ť	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	17716.0	0.76763	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

n, n, n, n, n, n, n, n, n, n, n, n, n, n		こ』こ	212	(.H.)	Ξ.	(m) H)	C = C (a)	ー (a) ンー・)	ල) ට	רון (פּ	(e)	(E) (-)
n ₁ n ₂ n ₃	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
7, 2,	_	2	1	3	2	1	1	1	1	1	1	1
2	0	0	0	2	-	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	- 0
	0.5	0,5	0.5	0.75	0.75	0.75	6,5	0.5	0.5	0.5	0.5	0.5
	-	-		~	1	1	1	1	1	-	-	1
	-	-	-	-	1	-	1	I	1	-	I	1
£,	17716.0	0.85395	0.85395	17710.0	17716.0	17716.0	0.91771	0.91771	0.91771	17716.0	0.91771	17716.0
	0	2	0	0	-	1	0	0	0	1	1	0
6,3	2	4	2	_		-	2	2	2	2	2	2
	0	0	0		2	1	0	0	0	0	0	0
	_	0.5	0.5	0.75	0.75	0.75	0.5	0.5	6.5	5.0	0.5	6.0
	-	-	-	-	-	1	1	1	1	1	1	1
V. (eV)	-30.19634	-111.25473	-35.08488	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	9.50874	23.87467	10,32968	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9,33352	9.37273	9.37273
T (eV)	7,37432	42.82081	10.11150	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V. (eV)	-3.68716	-21.41040	-5.05575	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3,45250	-3.38732	-3.45250	-3.45250
E(w no) (eV)	-14.63489	0	-14.63489	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15,35946	-15.35946
ΔΕ _{11,300} (30 110) (eV)	0	-2.69893	-2.69893	0	0	0	0	0	0	0	0	0
E. (40 110) (eV)	-14.63489	2.69893	-11.93596	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
E. (u_210) (aV)	-31.63534	-63,27074	-31.63541	-67,69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom - atom, msp^2, AO)$ (eV)	-1.44915	-2,69893	-1.65376	0	0	0	-1.85836	-1.85836	-1,44915	-1,85836	-1.44915	-1.44915
$E_{\tau}(so)(eV)$	-33.08452	-65,96966	-33,28912	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
@ (1015 rad / s)	16.4962	59,4034	24,3637	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9,43699	9.55643	9.55643
$E_{r}(eV)$	10.85807	39.10034	16.03660	16.40846	15.97831	15,91299	6.21159	6.21159	10.19220	6,21159	6.29021	6.29021
En (eV)	-0.21568	-0.40804	-0.26373	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16315	-0.16416	-0.16416
$\vec{E}_{knk}\left(aV ight)$	0.14655	0.21077	0.13638	0,35532 (Fg (13.458))	0.35532 (Fa (13.458))	0.35532 (Fa (13.458))	0.12312	0.17978	0.09944	0.12312 [2]	0.12312	0.12312
$\vec{E}_{\perp}$ (eV)	-0.14240	-0.30266	-0.19554	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Eme (cV)	0.14803	0.11441	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E. (Gray) (eV)	-33.22692	-66.57498	-33,48466	-67,92207	-49.80996	-31.70737	-33,59732	-33.49373	-33.24376	-33,59732	-33.18712	-33.18712
E (V) (or 10 10)	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489
Emster (c10 110) (aV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{D}(\epsilon_{Trimp})$ (eV)	3.95714	7.80660	4.21488	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734
Table 15 139. The total hond energies	of alkyl carbox	wlic acid anhydrid	les calculated usir	ig the functional g	oup composition	and the energies of	FTable 15,138 con	npared to the exp	erimental values [	İ		1
Formula Name $C-C(0)$ $C=O$ $C+O$	))C	0=2 (c	0-5	C'H'3	CHi	) ) - J H.	a) C-C (b)	(a)	C-C (d) C	ر (e) ر	C-C (f) Calculated Total Bond	ed Experimental nd Total Bond

	Relative Error	0,00013
	Experimental Total Bond Energy (eV)	36.948 81.401
	Calculated Total Bond Energy (eV)	56.94096 81.25636
	(t) 2~2	00
	(e)	0 0
CHILICITES TAILED	C-C (d)	0 0
מוכר ונו נוור העם	(e)	0.0
1 1 40 1 1 1 1 1 2 0 0 1 1	ر-ر (۹)	6 0
ic cricities of 1 an	( - C (a)	0 7
שניים ויים וויים	£	00
	CH,	0 7
	C'H'3	2 2
s calculated us	O-O Group	7 7
2010 2111 VOLUME	C=O Group	2
KVI Carboxy IC	C-C(O) Group	2 2
13. THE TOTAL DODG CHETTIES OF B	Name	Acetic anhydride Propanoic anhydride
200	Formula	C,H,O,

	Exp. 0		:	121.7 [36]	115.8 [36]	(acetrc anhydride)	(acclic anhydride)	101	(propane)	112 (propane) 113.8 (butane)	(isobutane)	111.0 (butane) 111.4	108.6 (acctyl chloride) 108.5	(acctone)		110.8	(Isobutane)	111.4	(tsobutanc)	(Isobulanc)
	Cal, 0	و		122.00	117.09	2,000	107.03	128.46	108,44	110.49		110.49	109,50		109.44	109.44	110.76	111.27	111.27	
	9	' ©	<u> </u>																	
	1 0	- ©	<u> </u>																	
(00.75)	θ	•	<u> </u>							69.51		69,51		1	70,36	/0.36				
_r (atom – atom, n	E,	(e _x ·		-1.44915	-1.85836	\$10PF 1"	1 (512)	0755011-	0				0			-1,85836	0	0	-1.85836	
ed. E ₇ is E	25			0,83339	0.78617	0.86445	02020	1 (570)	1.120				1.15796			0.81549	1.04887	1.04887	1.04887	
gle were us	5				-	-	-	6.75	Cl.				0.75			-	0.75	0.75	0.75	
receding an	"ტ			-	_	-	-	-   -					_			-	-	-	-	
rs from the	5				_	-	-	-					-			-	0.75	0.75	0.75	
the paramete	۲,	Atom 2		0.82562	0,78617	0.85395	0.85395	(eq. (15.114))					-			0.81549	0.91771	0.91771	17716.0	
nianon or 6,	<b>ሪ</b> '	Atom 1		0,84115	0,78617	0.87495	0,82562	0.86359					0.86359			0.81549	0.87495	0,87495	0.87495	
injuries and experimental values [1]. In the calculation of $\theta_j$ , the parameters from the preceding angle were used. $E_j$ is $E_j$ (atom – atom, msp² AO)	Atom 2 Hybridization	Designation	(Table 15.3.A)	21	36	0	0	н					I			23	_	-	_	
I I I I I I I I I I I I I I I I I I I	E contourse	Alam 2	TANK! XI	-16.47951	-17.30638	-13.61806	-13.61806	æ					æ			-16.68412 C.	-14.82575 C,	-14.82575 C	-14.82575 C.	
and and expand	Hybridization	Designation	(Table 15,3.A)	13	36	ç	31	7					7			25	'n	i.a	3	
A) 110 acres 41	Condombia	Vesti	16771 21.	0	-17.30638	-15,55033	-16.47951	-15.75493					-15,75493			-16.68412 C,	-15.35033	-15,55033	-15,55033	
	ZC Terminal	Aluns (a)		4.3012	4,4944	4,4944	4.6368	3.4252					3.4252			4.7958	4.1633	4.1633	4.7958	
	Sheed 2	(a _n )		2.63431	2.63431	2.63431	2,27954	2.11106		···			2.09711			2.91547	2.11323	2.09711	2.90327	
2	Hond I	( a ₀ )		2,27954	2.63431	2.86175	2.86175	2,11106			_		2.09711			2.91547	2 91547	2,91547	2.90327	
Alams of Angle 2	•			<i>'0'.5'07</i>	".)"()".)7	70°0'5	"O",)",)7	Methylene ZHC, H		'מ'מ'מ		H*.J".)7	H"HZ	`.'.'.'.'Z	H",)",))7	איז כ", כ" איז כ",	ZC, C, H iso C,	LC_C,H iso C,	ומו נ." אנ"נ."נ.	75.5.7

Table 15.140. The bond angle parameters of alkyl carboxylic acid anhydrides and expa

NITRILES 
$$(C_n H_{2n-1} N, n = 2,3,4,5...\infty)$$

The nitriles,  $C_n H_{2n-1} N$ , comprise a  $C \equiv N$  functional group, and the single bond of carbon to the nitrile carbon atom, C - CN, is also a functional group. The alkyl portion of the nitrile may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and 5 may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C - C bonds can be identified. The n-alkane C - C bond is the same as that of straight-chain alkanes. In addition, the C - C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C - C bonds comprise functional groups. The branched-chain-alkane groups in nitriles are equivalent to those in branched-chain alkanes.

The nitrile  $C \equiv N$  is solved equivalently to acetylene as given in the Acetylene Molecule section except that the energy for  $\Delta E_{H_2MO}(AO/HO)$  is two times that given in Eq. (14.343), 16.20002 eV, in order to match the N AOs to that of the nitrile  $C2sp^3$  HO having a bond order 15 of three.  $E_T(atom-atom,msp^3.AO)$  of the  $C \equiv N$  functional group is  $-1.56513 \, eV$  (Eq. (14.342)) corresponding to the third-order bonded  $C2sp^3$  HO.

The C-CN functional group is equivalent to that of an alkyl C-C group given in the Continuous-Chain Alkanes section except that  $E_T(H_2MO)$  and  $\overline{E}_{Kvib}$  are those corresponding to a nitrile. As given in the Continuous-Chain Alkanes section,  $E_T(atom-atom,msp^3.AO)$  of the 20 alkyl C-C group is  $-1.85836 \, eV$  where both energy contributions are given by Eq. (14.513). It is based on energy matching within the nitrile. It corresponds to the maximum-magnitude energy contributions of a single-bonded and a third-order bonded  $C2sp^3$  HO.

The symbols of the functional groups of nitriles are given in Table 15.141. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of nitriles are given in Tables 15.142, 15.143, and 15.144, respectively. The total energy of each nitrile given in Table 15.139 was calculated as the sum over the integer multiple of each  $E_D(cirosup)$  of Table 15.144 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the

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 $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of nitriles determined using Eqs. (15.79-15.108) are given in Table 15.146. The C of the  $C \equiv N$  group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene and alkynes.

Table 15.141. The symbols of functional groups of nitriles.	Group Symbol	C-C (i)	$C \equiv N$	$C \sim H$ $(CH_3)$	$C-H\left(CH_{s}\right)$	C-H	( - ( (a)	C-C (9)	(j-)	C~C (g)	() ~ () (e)	€ <u>0</u> 7.0
Table 15.141. The symbol	Functional Group	CCN	S	CH ₃ group	CH1 group	CH (alkyl) group	CC pond (n-C)	CC bond (iso-C)	CC bond (tert-C)	CC (iso to iso-C)	CC (t to t-C)	CC (t to iso-C)

Table 15.142.	The geometrical bu	and parameters of m	Table 15.142. The geometrical bond parameters of nitriles and experimental values [1]	tal values [1].							
rarameter	Group	Croup	$C-H(CH_j)$	$C-H(CH_2)$	C − H Group	C-C(a) Group	C~C(b) Group	C-C (c) Group	C - C (d) Group	C-C (e)	C~C (f)
$a\left(a_{v}\right)$	1.91255	1.20590	1.64920	1.67122	1.67465	2.12499	2.12499	2,10725	2.12499	2 10725	2 10725
$c'(a_0)$	1.38295	1.09813	1.04856	1.05553	1.05661	1.45744	1.45744	1,45164	1,45744	1.45164	145164
Bond Length $2c'(A)$	1.46365	1.16221	1.10974	1.11713	(.11827	1.54280	1.54280	1,53635	1.54280	1.53635	1.53635
Exp. Bond Length	1.468	1.159	1.107 (C-H propane)	1.107 (C-H propane)	1.122	1.532 (propane)	1,532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1,532 (propane)
<b>E</b>	familianal	(accioninisc)	(C - H butane)	(C-H butane)	(isobutane)	1,531 (butane)	1.531 (butane)	1.531 (butane)	1,531 (butane)	1.531 (hrtfane)	1.531
$h,c(a_0)$	1.382110	0.49828	1.27295	1.29569	1.29924	1.54616	1.54616	1,52750	1.54616	1.52750	1 57750
g	0.72309	0.91064	0.63580	0.63159	0.63095	0.68600	0.68600	0.68889	0 69600	000070	000000

1

	1					Einel Total	,		F	1 11	, o	9	d	P	-
Bond	Arom	<i>L</i> ₇	7.7	2,7	7.	Transition	funnal	final	Conform	E (C.25p')	<b>.</b>	<b>5</b>	5":	; ;	
		(eV) Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	(72 <i>sp</i> )	(a _n )	(a ₀ )	(ev) Final	(eV) Final	<u> </u>	<u> </u>		(a _a )	(%)
RH,C,C = N	>	-0.78257	0	0	C		0.93084	0.87170	-15.60832		147.01	32.99	72.28	0,36699	0.73114
RH,C,C, = N	ڹ	-0.78257	-0.92918	0	0	-153,32744	17710.0	0.82272	-16.53750	-16.34664	145.42	34.58	69.58	0.42077	0,67736
RH ₂ C _b - C _a N	J.	-0.92918	-0.78257	c	0	-153.32744	17710.0	0.82272	-16.53750	-16.34664	81.32	98.68	38.00	1,50718	0.12423
H,C,-C,N	ڻ.ٰ	81626'0-	0	0	0	-152,54487	17716.0	0.86359	-15.75493	-15.56407	85.50	94.50	40.67	1,45066	0,06771
$RH_2C_rH_2C_o-C_aN$ $R=alkyl$	ປ	-0.92918	81626.0-	o	0	-153,47406	17716.0	0.81549	-16.68412	-16,49325	80.53	99.47	37.51	1.51718	0.13423
C-H (CH ₃ )		-0.92918	0	0	c	-152.54487	17716.0	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1,23564	0.18708
$C-H$ $(CH_1)$	Ü	-0.92918	-0.92918	0	0	-153,47406	17716,0	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
C - H (CH) (ii)	υ ·	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0,77247	-17,61330	-17.42244	61.10	118.90	31.37	1,42988	0.37326
$H_3C_aC_bH_2CH_3 (C-C_5C_3)$	ບໍ	-0.92918	0	o	0	-152.54487	12/16/0	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1,83879	0.38106
$H_3C_4C_4H_1CH_2 - (C_4C_5)$	ڻ	-0.92918	816260-	O	0	-153,47406	17716.0	0.81549	-16,68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R - H_2(C_s(H_1C_s - R)HCH_1 - C_s - C_b)$	ڻ	-0.92918	-0.92918	-0.92918	О	-154,40324	17716'0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1,97162	0.51388
$R - H_1C_a(R' - H_1C_a)C_b(R'' - H_1C_c)CH_1 - (C - C C)$	ڻ	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$k \alpha C_s C_s (H_s C_c - R^s) H C H_s - (C - C_s (d))$	້ ບໍ	-0,92918	-0.92918	-0.92918	Ð	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1,97162	0.51388
$ter(C_n(R^n - H_1C_n)C_n(R^n - H_1C_n)CH_2 - (C - C_1C_n)$	ڻ	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
teric $C_s(H_1C_s-R)HCH_1-$ (C = C (f))	ڻ	-0.72457	-0.92918	-0.92918	-0	-154.19863	0.91771	0.78155	-17,40869	-17.21783	52.78	127.721	24,04	1.92443	0.47279
$isoC_{*}(R'-H_{2}C_{s})C_{h}(R''-H_{2}C_{s})CH_{2} (C-C^{*}(f))$	ڻ	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.143. The MO to HO intercept geometrical bond parameters of nitriles. R,R',R'' are H or alkyl groups.  $E_T$  is  $E_T(anom-alom,msp^2,AO)$ .

rarameters	C-C (i) Group	C≡ N Group	CH, Group	CH ₂	C – H Group	C-C(a) Group	('-(' (b) Group	C – C (c) Group	C – C (d) Group	(; –C; (e)	(J-C)
n,	-		3	2	-	-	_		-	-	dian
$n_2$	0	0	2	-	0	0	0	0			-   -
П,	0	0	0	0	0	0	0	0	0		0
C ₁	5.0	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	30	0.5
C ₂	-	1	-	_	_	_	1	-	-	25 -	3 -
ς,	-	1	1	-	-	-	_	1			-   -
$c_i$	0.91771	0.91140	0.91771	17710	0.91771	0.91771	0.91771	0.91771	0 91771	0.91771	0.01771
ر. ا	0	_	0	-	-	0	0	0	-	1	0.71711
<i>c</i> *	2	9	-	-	-	2	2	2	2	2	2
<b>5</b>	0	0	3	2	-	0	0	0	0	0	0
ָרָ <u>י</u>	0.5	0.5	0.75	0,75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
( 2,0	-	-	-		-	1	1	_	1	-	_
F _c (eV)	-33.01231	-207.49229	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V _p (eV)	9,83824	37.16984	38.92728	25.78002	12.87680	9.33352	9.33352	9,37273	9.33352	9.37273	9.37273
1 (eV)	8.63043	86.03250	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
/" (eV)	-4.31522	-43.01625	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
# (av.m) (eV)	-14.63489	32.40004	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
( A2) (40.10) (4A)	-1.85837	0	0	0	0	0	0	0	0	0	0
$E_{T}(AO BO)$ (eV)	-12.77652	32.40004	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(n_2no)$ (eV)	-31.63537	-94.90616	-67.69451	-49,66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_r(atom - atom, msp^3.AO)$ (eV)	-1.85836	-1.56513	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_r(\omega)$ (cV)	-33.49374	-96.47124	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
@ (10" rad/s)	19.2516	22.0753	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_{\kappa}(eV)$	12.67172	14.53031	16.40846	15.97831	15.91299	6.21159	6:21159	10.19220	6.21159	6.29021	6.29021
$E_{D}$ (eV)	-0.23588	-0.24250	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$L_{K10}$ (eV)	(37]	0.28107	0,35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978	0.09944	0.12312	0.12312	0.12312
$E_{\alpha c}$ (eV)	-0.17884	-0.10197	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0,10359	-0.10260	-0.10260
$L_{max}(eV)$	0.14803	0.14185	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$L_T(Group)(eV)$	-33.67258	-96.77713	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
C _{initial} (e ₁ 10·110) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Emma (q, 10 HO) (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$\mathcal{L}_D$ (Grown) (GV)	4.40280	8.82594	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.145. The total bond energies of nitries calculated using the functional group composition and the energies of Table 15.144 compared to the experimental values [3]. The magnetic energy E_{ms} that is subtracted from the weighted sum

(Group)	Relative Error		0.00174	0.00171	0.00082	0.00092	111000	-0.00122	70,000	0.0000	0.00069
sum or me $\mathcal{L}_L$	Experimental	I olal Bond Energy (eV)	25.77	37.94	50.08	50.18	96 69	07 (9	05 98	22.00	123.05
(a,b) (eag) (eag) (eb)	Calculated	Energy (eV)	25,72060	37,87830	50,03600	50.13689	62,19370	62 47823	86 50910	08 66680	122.98220
anomarica III	Ema	•	0 1	0	0	0	0	·	0	c	
Ci mus Sumi	(J) 2-2		0 (	<b>5</b> 1	0	c	0	0	0	0	0
3	(e)		٥ د		<b>5</b>	0	0	c	0	0	o
	C-C (q) C-C (e)		> 0		٥ «	<b>c</b> (	-	0	c	0	0 0
	(2)	6				2 6	3 (	· •	0	c	
	C-C (b)	0	. 0			4 6	> <	0 (	0	۰,	¢ c
	C-C'(a) $C-C'(b)$	0	-	۲		. ~	. =	2 4	٠,	٥:	× 27
	H.)	С	0	c	_	· c	. =		= 0	- 0	- 0
	C.H.	o,	-	7	5	Э	=	. •	, •	. >	o 27
	CH ₃	-	_		7	-	~	_	_		
	$C \equiv N$ Group	_	_	-	_	_	_	_	-		
15.58).	C-C (i) Group	_			_			<b>-</b>		_	
llues based on composition is given by (1	Name	Acetonitrile	Tropanentrie	2 Methodisciple	z-ivienty/proparentinie	Penlanentinie	2.2-Dimethylpropanentrile	Heptanenitrile	Octanentrile	Decanentrile	Tetradecanenitrile
values base	rormuia	Z, H.S.	2.25		NG I	Net 2	ולים אינו אונו	Z, E	Z,H.C	CloHtoN	CuHTN

5 Table 15.146. The bond angle parameters of nitriles and experimental values [1]. In the calculation of  $\theta_p$ , the parameters from the proceeding angle were used.  $E_T$  is  $E_T$  (atom – atom, msy', AO).

		,						·										
Exp. θ (°)				109.7 (acetonitrile)	107 (propane)	112 (propane) 113.8 (butane)	(IO.8	111.0 (butane)	(isobutane)	108.5 (acetone)			110.8	(isobutane)		III.4	111.4	(isobutane)
Cal. <i>θ</i>		180	109.50	109.44	108.44	110.49		110.49		109.50	109.44	109.44	110.67	77 011		111,27	111.27	
<i>6</i> . ©																		
(°)																		
0, O				70.56		69.51		15.69			70.56	70.56						
$E_T$ (eV)			0		0					0			-1.85836	0		0	-1.85836	
°,			1.157%		1.15796					1.15796			0.81549	1.04887		1.04887	1.04887	
5			0.75		0.75					0.75			_	0.75		0.75	0.75	
<i>5</i>			-		-				٠	-			_	-		_	-	
ڻ -					-					-				0.75		0.75	0.75	
C ₂ Atom 2			-		-					-			0.81549	17716.0		0.91771	17710.0	
C ₂			0.86359		0.86359					0,86359			0.81549	0.87495		0,87495	0.87495	
Hybridization Designation	(Lable 15,3,A)		6		Ξ				:	E			25	_		-	_	
L'intonbre Aton 2		3			±				:	=		21110	-۱۵،۵۳۹۱۲ ر	-14.82575 C.,	-14.82575	ڻ"	-14.82575 C.	
Hybridization Designation	(Liable 19.3.A)	7			7				-	-			23	, ,,	,		5	
L'endouple Atom I		-15.75493			-15.75493				15 75.403			-16 68417	ڻ.	-15.55033 C,	-15.55033	*	-15.55033	
Teminal Atoms (a ₀ )		3.4252			7675'6	_			3.4252				4.7958	4.1633	4.1633		4.7958	
(a)		2.09711		11100	2.111/00				2,09711				2.91547	2.11323	2,09711		2,90327	
13mul 1 (a ₀ )		2,09711		201116	041117				2.09711				2.91547	2.91547	2.91547		2.90327	
	N".)7,	ZHC, H	ZHC.C.	Methylene	ZH( "H	°,7",7",7		ДС,С,Н	Methyl / H/	J'.)", J	ZC,C,H	70,00	iso ("	ZC,C,H in C,	Н"Э"Э7	[s] (a)	کرد,رد نما ('ر	ZC,C,C,

THIOLS 
$$(C_n H_{2n+2} S_m, n = 1, 2, 3, 4, 5...\infty)$$

The alkyl thiols,  $C_n H_{2n+2} S_m$ , comprise a SH functional group and a C-S functional group. The alkyl portion of the alkyl thiol may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in thiols are equivalent to those in branched-chain alkanes.

The parameters of the SH functional group is solved using Eq. (15.41). As in the case of the C-H bonds of  $CH_n$  n=1,2,3, the S-H-bond MO is a partial prolate spheroid in between the sulfur and hydrogen nuclei and is continuous with the S3p shell. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of the S3p shell and comprises 75% of a  $H_2$ -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Since the energy of S,  $E(S) = -10.36001 \ eV$ , is less that that of H, the linear combination of the  $H_2$ -type ellipsoidal MO with the S3p shell further comprises an excess 50% charge-density donation from H to the S3p shell of the S-H-bond MO to achieve an energy minimum. The initial total energy of the shell is given by the sum over the four 3p electrons. From Eq. (15.12), the sum  $E_T(S,3p)$  of the energies of S,  $S^+$ ,  $S^{2+}$ , and  $S^{3+}$  [38] is

$$E_T(S,3p) = 10.36001 \ eV + 23.33788 \ eV + 34.79 \ eV + 47.222 \ eV$$

$$= 115.70989 \ eV$$
(15.118)

By considering that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{3p}$  of the S3p shell may be calculated from the Coulombic energy using Eqs. 25 (15.13) and (15.118):

$$r_{3p} = \sum_{q=12}^{15} \frac{(Z-q)e^2}{8\pi\varepsilon_0 \left(e115.70989 \ eV\right)} = \frac{10e^2}{8\pi\varepsilon_0 \left(e115.70989 \ eV\right)} = 1.17585a_0 \tag{15.119}$$

where Z=16 for sulfur. Using Eqs. (15.14) and (15.119), the Coulombic energy  $E_{Coulomb}(S,3p)$  of the outer electron of the S3p shell is

$$E_{Condomb}(S,3p) = \frac{-e^2}{8\pi\epsilon_0 r_{3p}} = \frac{-e^2}{8\pi\epsilon_0 1.17585a_0} = -11.57099 \ eV$$
 (15.120)

The sharing of the electrons between the S and H atoms permits the formation an S-H-bond MO that is lowered more in energy than the participating S3p orbital which consequently increases in energy. By considering the 50% electron redistribution in the S-H group as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{S-H3p}$  of the S3p shell may be calculated from the Coulombic energy using Eq. (15.18)

$$r_{S-H3p} = \left(\sum_{n=12}^{15} (Z-n) + 0.25\right) \frac{e^2}{8\pi\varepsilon_0 \left(e115.70989 \, eV\right)}$$

$$= \frac{10.5e^2}{8\pi\varepsilon_0 \left(e115.70989 \, eV\right)}$$

$$= 1.23465a_0$$
(15.121)

where the s=-1 in Eq. (15.18) due to the charge donation from H to S. Using Eqs. (15.19) and (15.121), the Coulombic energy  $E_{Coulomb}(S_{S-H},3p)$  of the outer electron of the S3p shell is

$$E_{Coulomb}(S_{S-H}, 3p) = \frac{-e^2}{8\pi\varepsilon_0 r_{S-H3p}}$$

$$= \frac{-e^2}{8\pi\varepsilon_0 1.23465a_0}$$

$$= -11.01999 eV$$
(15.122)

Thus,  $E_r(S-H,3p)$ , the energy change of each S3p shell with the formation of the S-H-bond MO is given by the difference between Eq. (15.120) and Eq. (15.122):

$$E_{T}(S-H,3p) = E(S_{S-H},3p) - E(S,3p)$$

$$= -11.01999 \ eV - (-11.57099 \ eV)$$

$$= 0.55100 \ eV$$
(15.123)

15 Then, in Eq. (15.42):

$$E_{T}(AO/HO) = E(S) - E_{T}(S-H,3p)$$

$$= -10.36001 \ eV - 0.55100 \ eV$$

$$= -10.91101 \ eV$$
(15.124)

And, in Eq. (15.56),

$$E_r(atom - atom, msp^3.AO) = 0.55100 \text{ eV}$$
 (15.125)

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Due to the charge donation from H to S,  $c_1 = 1$  in both Eqs. (15.42) and (15.56). As in the case of the C - H-bond MO,  $C_1 = 0.75$  based on the orbital composition. In alkyl thiols, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is also one, and the energy matching condition is determined by the  $C_2$  parameter. Using the energy of S,  $E(S) = -10.36001 \ eV$  in Eq. (15.65), the hybridization factor  $C_2$  of Eq. (15.52) for the S - H-bond MO is

$$C_2(S3p \text{ to } H) = \frac{E(S, 3p)}{E(H)} = \frac{-10.36001 \text{ eV}}{-13.60580 \text{ eV}} = 0.76144$$
 (15.126)

Since the energy of S is matched to the Coulombic energy between the electron and proton of  $E(H(a_0))$ ,  $E(H(a_0)) = E(H(a_0)) = -13.60580 \ eV,$ 

- 10  $E_{initial}(c_s \text{ AOIHO}) = E(H) = -13.59844 \text{ eV}$ , and  $E_{mag}$  is that corresponding to  $E(H(a_0))$  given by Eq. (15.58).  $E_D(Group)$  for hydrogen sulfide is equivalent to that of the SH functional group, and the  $E_D(Group)$  (eV) for dihydrogen sulfide follows the same derivation as that for the SH functional group except that the parameters correspond to  $n_1 = 2$  rather than  $n_1 = 1$  in Eqs. (15.42) and (15.56).
- Furthermore, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the C-S-bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with E(AO/HO)=0 and  $E_T(AO/HO)=\Delta E_{H_2MO}(AO/HO)$ . Then, the solution of the C-S functional group comprises the hybridization of the 2s and 2p AOs of C to form a single  $2sp^3$  shell as an 20 energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the S AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243),  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. Then,  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a 25 corresponding energy of  $E(C,2sp^3)=-14.63489~eV$  (Eq. (15.25)), and the S AO has an energy of E(S)=-10.36001~eV. To meet the equipotential condition of the union of the

C-S  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.51) for the C-S-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ S\right) = \frac{E(S)}{E(C,2sp^3)}c_2\left(C2sp^3HO\right) = \frac{-10.36001\ eV}{-14.63489\ eV}(0.91771) = 0.64965 \quad (15.127)$$

Since the sulfur is energy matched to  $E(H(a_0))$  in the S-H-bond MO,  $E_T(atom-atom, msp^3.AO)$  of the C-S-bond MO in Eq. (15.52) due to the charge donation from the C and S atoms to the MO is -0.72457~eV corresponding to the energy contribution equivalent to that of a methyl group (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl thiols are given in Table 15.147. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl thiols are given in Tables 15.148, 15.149, and 15.150, respectively. The total energy of each alkyl thiol given in Table 15.151 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.150 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The C-C bonds to the HCSH group (one H bond to C) were each treated as a tert-butyl C-C.  $E_{mag}$  was subtracted for each t-butyl group. The bond angle parameters of alkyl thiols determined using Eqs. (15.79-15.108) are given in Table 15.152.

| Table 15.147. The symbols of functional groups of alkyl thiols. | Eumetional Group | Group Symbol | SH group | SH group | SH group | SH group | SH group | SH group | SH group | SH group | C - H (CH₃) | CH₃ group | C - H (CH₃) | CH₃ group | C - H (CH₃) | C - G (a) | CC bond (n-C) | C - C (a) | CC bond (n-C) | C - C (b) | CC bond (n-C) | C - C (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | CC (c) | C

	C-H Group
	$C-H$ $(CH_1)$
tal values [1].	$C \sim H\left(CH_3\right)$
thiols and experimen	C-S Group
d parameters of alkyl	SH. Group
The geometrical bon	$S-H(H_2S)$
15.148.	meter

	_		_		_	_	т			_	_	_	_	_	-		٠,
	(t)	cronb		2.10725		1.45164		1.53635		1.532		(propane)	1,531	(Antone)	Contained	1.52750	
	(e) <i>D- D</i>	dioip diame	2000.0	7.107.5		1.45164		1.53635		1.532	(consess)	(propare)	1.531	(hutane)	(Aurana)	1.52750	
	(g) ひ-ひ	ding	20771	2,12499	.,	1.45/44	occes.	1.54280		1.532	(nronana)	(probanc)	1.551	(butane)		1.54010	20,000
	(c) C = C (d)	discip	2 10725	77/01.7	1 45174	1.45104	1,620.2	1.33033		1.532	(propage)	1531	155.1	(butane)	1 57750	00/70	000000
	Group Group		2 12499		1 15711	1,47,74	1 54280	004401	965 .	755.1	(propane)	1 531	100.1	(butane)	1 5/8/16	010101	000000
1	Group		2.12499		1 45744		1 54280		1 527	750-1	(propane)	. 1531	***************************************	(butane)	1 54616	2701.011	0.68600
-	Group		1.67465		1.05661		1.11827				1.122	(isobutane)			1.29924		0.63095
11 (211)	$C = H \left( CH_2 \right)$	Ciono	1.67122		1.05553		1.11713		101	17	(c - u bropane)	1.117	(C = H buttons)	(alimina)	1.29569	07.07.0	0.03139
	$C = B \left( C B_3 \right)$	Group 67122		74040	1.04856		1.10974		1.107	(C-H promon	(c - 1) propane)	1.117	(C-H butane)	(Cump)	1.27295	003620	0.03300
ĵ	Group		57606.1	1 71455	1.71455		1.81460		1.819	(methanethiol)	(Ioungum)		(ethanethiol)		0.84112	0.80770	0,170.0
	Group	1 0227	70/52.1	1 269.17	740071		1.34244		1.34066	(hydrogen sulfide)	(2000)	40.	(methanethiol)		1.32964	50050	0.000
C	(41.)	1 02763	70/50.1	1 26842	71.007		1.34244		_		9555.1	-		1 2000 1	50675	0.69025	
		00	(0,1)	c. (a.)	/# /	Bond Length	2c' (A)		Exp. Bond	Lenvih		7	, ,	1 (2)	(n) 2'n	9	

Bond	Atom	E,	E,	E,	$E_{\tau}$	Final Total	, minel	Jan.	Erratous	$E(C2sp^3)$	.θ	9,	θ,	ď	4,
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy $(7.5p^3)$ (eV)	(a _e )	(a ₀ )	Final (eV)	(eV) Final	<u> </u>	• •	©	(°°)	(a _o )
S ~ H (hydrogen sulfide)	×	0.55100	0	c	o		1.32010	1.23465	-11,01999		108,65	71.35	61.62	0.87355	0,39487
(dinydrogen suifide)		-0.36229	0,55100	0	0		1,32010	0.92955	-14.63704		62.78	92.91	44.28	131557	0.04714
C.H. – 3H	:S:	-0.36229	0,55100	0	0		1,32010	0.92955	-14.63704		132,06	47.94	55.13	1.09181	0.62274
C.H. – SH	ئ	-0.36229	e	0	0	-151,97798	17716.0	0.89582	-15.18804	-14.99717	69.84	110.16	88.87	0.03762	1,67692
RC H2C,H2 - C,H,SH	٠٠	-0.36229	-0,92918	c	0	-152,90716	17710,0	0.84418	-16.11722	-15.92636	128.69	51.31	51.57	1.18689	0,52765
C-H (C'H ₃ )	·	0.92918	0	0	0	-152,54487	12216'0	0.86359	-15.75493	15.56407	77.49	102.51	41.48	1,23564	0.18708
$C-H(CH_2)$	ن	-0.92918	-0.92918	0	0	-153,47406	17716.0	0.81549	-16.68412	-16.49325	68.47	111.53	35,84	1.35486	0,29933
('-H (C'H)	٠	-0.92918	-0,92918	-0.92918	D	-154,40324	17710.0	0.77247	-17.61330	-17.42244	61.10	118,90	31,37	1.42988	0,37326
$H_3C_CH_3C_H_2$	ئ ر	-0.92918	0	0	0	-152.54487	17716.0	0.86359	-15.75493	-15,56407	63.82	116.18	30,08	1.83879	0.38106
$H_1^{\zeta}C_2^{\zeta}C_1H_2^{\zeta}H_2^{\zeta} - (\zeta^{-1})$	. t	-0.92918	-0.92918	0	0	-153.47406	17716.0	64518.0	-16,68412	-16,49325	56,41	123.59	26.06	1.90890	0,45117
$R - H_2(C_aC_b(H_2C_b - R))HCH_2 - (C - C_b)$	ئ *	-0.92918	-0,92918	-0,92918	Đ	-154,40324	17716.0	0.77247	-17,61330	-17,42244	48.30	131.70	21.90	791161	0.51388
$R - H_2(C_s(R - H_2C_s)C_s(R^n - H_2C_s)CH_2 - (C - C_s(s))$	<u></u>	-0.92918	-0,72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$i ko C_{\alpha} C_{\alpha} \left( H_{\alpha} C_{\alpha} - R^{\alpha} \right) H C H_{\alpha} - \left( C - C^{\alpha} \left( A \right) \right)$	ť	-0.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$\lim_{C \to C} (R' - H_2C_4)C_6(R'' - H_2C_2)CH_2 - CC + CC_2 + CC_3$	ڻ	-0,72457	-0.72457	-0.72457	-0.72457	-154.51399	12210	0.76763	-17,92866	-17,73779	50.04	129.96	22.66	1.94462	0.49298
$lur(C_{s}C_{h}(H_{2}C_{s}-R))HCH_{2}-(C-C_{s}(f))$	ئ.	-0.72457	-0.92918	-0.92918	. <del>0</del>	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0,47279
$ispC_{\sigma}(R^{*}-H_{2}C_{\sigma})C_{\sigma}(R^{*}-H_{2}C_{\sigma})CH_{2}-(C-C^{*}(f))$	Ċ,	-0.72457	-0.72457	-0.72457	-0.72457	-15451399	17716.0	0.76765	-17.92866	-17.75779	50.04	129.96	22.66	1.94462	0.49298

Table 15.150. The energy parameters (eV) of functional groups of alkyl thiols.	ers (eV) of function	mal groups of alky	of thiols.									9,0
Parameters	H.S	SH Group	رسال Group	CH,	CH,	C-H Group	Croup	C-C (b) Group	Group Group	Group	Group	Group
The state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the s	2	-   _	_	3	2	-	-	-	-	-	-	1
	0	0	0	2	_	0	0	0	0	0	0	0
n,	0	0	0	0	0	0	0	0	0	0	0	0
	0.75	0.75	0.5	0.75	0.75	0.75	5,0	0.5	0.5	0.5	0.5	0.5
(;	0.76144	0.76144	0.64965	-		1	1	1	1	1		-
	-	-		1	-	1	_	1	1	1	1	1
5	-		-	0.91771	0.91771	0.91771	0.91771	0,91771	0.91771	0.91771	0.91771	0.91771
	. 2	-	0	0		_	0	0	0	1	-	0
6,	_	-	2	-	_		2	2	2	2	2	2
7	-	-	0	3	2	_	0	0	0	0	0	0
	0.75	0.75	0.5	0.75	0.75	0.75	6.5	6.5	0.5	0.5	0.5	0.5
(;	0.76144	0.76144	0.64965	-	-	-	-	_	1	1	1	-
V (eV)	-72.80662	-36.40331	-46.36495	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V (eV)	21.45310	10.72655	7.93551	38,92728	25.78002	12.87680	9.33352	9,33352	9.37273	9.33352	9.37273	9.37273
T' (eV)	19,81003	9.90502	12,13899	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	00506'9	6.90500
V_ (eV)	-9.90502	4.95251	-6,06949	-16,26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3,38732	-3.45250	-3.45250
El.to nol (eV)	-20.72002	-10,36001	0	-15,56407	-15.56407	-14.63489	-15,56407	-15.56407	-15.35946	-15,56407	-15.35946	-15.35946
DEnam (w no) (eV)	1,10200	0.55100	-0.72457	0	0	0	0	0	0	0	0	0
E. [ to 110] (eV)	-19.61802	-10.91101	0.72457	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
E, (u, sia) (eV)	-63.27052	-31,63526	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31,63537	-31.63535	-31.63537	-31,63535	-31.63535
E_ (atom - atom, msp², AO) (eV)	1.10200	0.55100	-0.72457	0	ò	0	-1,85836	-I.85836	-1,44915	-1.85836	-1.44915	-1.44915
$E_{\tau}(xo)$ (eV)	-62.16874	-31.08437	-32,35994	-67.69450	-49.66493	-31.63537	-33.49373	-33,49373	-33.08452	-33.49373	-33.08452	-33.08452
w (101s rad 1s)	12.5415	12.5415	30.5436	24,9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E. (eV).	8.25504	8.25504	20.10434	16,40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
Ē. (eV)	-0.17669	-0.17669	-0.28705	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Extra (eV)	0.32422	0.33620	0.08146	0,35532 (Fa (13,458))	0,35532 (Fa (13.458))	0.35532 (Fq. (13.458))	0.12312	0.17978	0.09944	0.12312 [2]	0.12312	0.12312
E (eV)	-0.01458	-0.00859	-0.24632	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E (aV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E. (cray) (eV)	-31.10493 ^a	-31.09296	-32.60626	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33,59732	-33.18712	-33.18712
E (c, 10 110) (eV)	-13.60580	-13.60580	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
E (c, 10' 110) (eV)	-13.59844	-13.59844	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
En (inner) (eV)	3,78628	3.77430	3,33648	12.49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734
									!			

a  $E_T(n-s,n_s) = E_T(n_s) - E_T(ms) = 62.19789 \text{ eV} - \left(-31.09296 \text{ eV}\right)$ .

Table 15.151. The total bond energies of alkyl thiols calculated using the functional group composition and the energies of Table 15.150 compared to the experimental values [3]. The magnetic energy E that is subtracted from the weighted sum of the E_o( $\omega_{ee}$ ) (eV) values base

Compositio	composition is given by (15.58).												ř		0	- no	Frame ( .a) (A-m)0
Formula	Name	SH	HS	2-7	7.,		14.7	1000	1000								
		i.,	Group.	ָ פַּ	, u	; ;	5	(a)	(a) C=C (b)	(6)	C→C (d)	(a) (プー)	C-C (f)	ij	Calculated	Experimental	Relative Error
		Group	Group	dinoto										Sou.	Total Bond	Total Bond	
H2	Hydrogen Sulfide	_		0	0	0									Energy (eV)	Energy (eV)	
S.H.	Dihydrogen Sulfide	0	_	0	0				- 0		<b>-</b>	0	0	0	3.77430	3.653	-0,03320
CH ₁ S	Methanethiol	Đ	_		-			> <	<b>&gt;</b> (	<b>-</b>	0	0	0	.0	7.56058	7.605	0.00582
C.H.S	Ethanethiol	0		_	-	-		<b>-</b>	- 0	<b>-</b>	0 1	0	0	0.	19.60264	19.575	-0.00141
C'H.S	I-PropanethioI	c	_			٠,			- 4	0 0		0	0	0	31,76034	31.762	0.00005
CHES	2-Propanethiof	0	_	_	. 7	1 0		۹ د		٥ ،	ъ.	0	0	0	43.91804	43,933	0,00035
CHINS	1-Butanethiol	c	-	_	-	: (*		2 .	7 0	-	0	o	0		44.01893	44.020	0.00003
CHINS	2-Butancthiof	0	_			· -	- c	٦-	0 (	0 1		0	0	0	56.07574	56.089	0.00024
C.H ₁₀ S	2-Methyl-1-propanethiol	0	_	-	10				7 (	0 (	0	0		0	56.17663	56.181	0 00000
SE E	2-Methyl-2-propanethiol		-	_	1 (4		~ c	> <	n 6	۰ د	0	0	0	0	56,14830	56.186	990000
CsH ₁₂ S	2-Methyf-1-butanethiol	0	_	_	. 6			- c	<b>-</b> (	n	e (	0	0	÷	56,36027	56.313	-0.00084
CsHrs	1-Pentanethiof	0	_		-	1 -0	- =		2 6	۰ د	0	0	0	0	. 0090289	68.314	0.00012
CsHrs	2-Methyl-2-butanethiol	0	-	_	· in	. –	e c	+ -	<b>-</b>	۰ م	0 (	0	0	0	68,23344	68,264	0.00044
CARIS	3-Methyl-2-butanethiol	0	_	_	'n	• =		<b>→</b> <	> 0	n (	φ.	0	0	<del>,</del>	68,51797	68,441	-0.00113
CAHIS	2.2-Dimethyl-f-propanethiol	0	_		·		ء د	o •	กซ	<b>=</b> (		0	0	¢	68.31552	68,381	0.00095
C,H,1,S	I-Hexanethiof	0		_	. –	,		- 14		n :	0	0	0	÷	68,51797	68.461	-0 000K4
C,H,IS	2-Methyl-2-pentanethiol	0		_		, ~	2 6	٠.	3 5	٥,	0	0	0	0	\$0,39114	80,416	0.00031
CoH14S	2.3-Dimethyl-2-butanethiol	0	_	_	। <del>च</del>	) C		7 0	<b>=</b> (	<b>n</b> (	0	0	0	÷	80,67567	80,607	-0.00085
C,H ₁ ,S	I-Heptanethiol	0		_	_	: 12	- c	= 4	7 5	7 0	0 (	0	_	, 7	80,71992	80,603	-0.00145
C.mH.3	I-Decanethiol	c	-		_	: 50				۰.۰		0 (	0	0	92.54884	92.570	0.00023

Table [5.132. The bond angle parameters of alkyl thiols and experimental values [1]. In the calculation of  $\theta_c$ , the parameters from the preceding angle were used. E, is E, (atom - atom, msy', AO).

,														
$ (\circ) $	96.5 (methanethiol) 96.4	(cthancthiol) 108.3	107	(propane) (propane) 113.8 (butane) 110.8	(September 111.0 (Butane)	(isobutane)			110.8	(isobulane)	111.4	(1500utanc)	(isobutane)	
Cal. θ	97.28	110.92	108.44	110.49	110.49	109 50	2	109.44	109.44	110.76	111.27	111.27		107.50
(°)														
(°)														
6,0				15.00	69.51		25.55	8 1	70.36					72.50
$E_{\tau}$ (eV)	0	-0.72457	0	,		0			-1.85836	0	0	-1.85836		
33	1.13415	0.73257	1.15796			1.15796			0.81549	1.04887	1.04887	1.04887		
٠ ٠	0.75		0.75			0,75			-	0.75	0.75	0.75		
౮'	-	0.64965 (Eq. (15.127))	_			_			-	-		-		
i.	0.75	-	-			-			-	0.75	0.75	0.75		
C ₂ Alon 2	0.86359	0.64965 (Eq. (15.127))	-			-			0.81549	17716.0	17710,0	17710.0		
C ₂ Atlan f	0.76144 (Eq. 15.125))	0.81549	0.86359			0,86359			0.81549	0.87495	0.87495	0.87495		
Atom 2 Hybridization Designation (Table	S	S	н			x			25	-	-	-		
F. Crestowske Aton 2	-15.75493	-10,36001 S	π			I			-16.68412	-14,82575	-14.82575 .C.	-14.82575 (°,		
Atom I Hybridization Designation (Table 15 3.A)	7	ĸ	7			7			25	5	1/2	· v		
L'Euntembe Atom I	-10.36001	-16,6841 <u>2</u> C,	-15.75493			-15.75493			-16.68412 C,	-15,53033	-15.55033 C,	-15.55033		
2c' E. Terminal Atoms (a ₀ )	4,5166	5.2344	3,4252			3,4252			4,7958	4.163	4.1633	4.7958		
2c' Bend 2 (a ₀ )	3,42910	3,42910	2.11106			2.09711			2.91547	2,11323	2.09711	2.90327		
2c' 19end 1 (a ₀ )	2.53685	2.91547	2.11106			2,09711			2.91547	2.91547	2,91547	2,90327		
	*.WHZ	S".J".)7	H´.)HZ	, ZC, C, C;	H,C,"C,H	Methy I ZHC "H	7۲.۴۲.	4C,C,H	خر'ڊر"ر' نبه ر"	LC, C', H iso C',	Z(',C',H isa C',	الما لا م	7C,C,C,	

SULFIDES 
$$(C_n H_{2n+2} S_m, n = 2,3,4,5...\infty)$$

The alkyl sulfides,  $C_n H_{2n+2} S_m$ , comprise two types of C-S functional groups, one for t-butyl groups corresponding to the C and the other for the remaining general alkyl groups including methyl. The alkyl portion of the alkyl sulfide may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in sulfides are equivalent to those in branched-chain alkanes.

Each C-S group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the S AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243),  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. As in the case of thiols,  $C_2$  of Eq. (15.52) for the C-S-bond MO given by Eq. (15.127) is  $C_2(C2sp^3HO\ to\ S) = 0.64965$ .

The C-S group of alkyl sulfides is equivalent to that of thiols where  $E_T(atom-atom, msp^3.AO)$  is -0.72457~eV (Eq. (14.151)). The t-butyl-C-S group is also equivalent to that of thiols except that the energy parameters corresponding to the oscillation in the transition state are matched to those of the t-butyl group.

The symbols of the functional groups of branched-chain alkyl sulfides are given in Table 15.153. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfides are given in Tables 15.154, 15.155, and 15.156, respectively. Consider that the C-S bond is along the x axis in the xy-plane. The S nucleus is at the focus +c and the C nucleus is at the focus -c. The elliptic angle  $\theta$ ' is taken as counterclockwise from the x-axis for S and as clockwise from the -x-axis for C. The total energy of each alkyl sulfide given in Table 15.157 was calculated as the sum

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over the integer multiple of each  $E_D(Group)$  of Table 15.156 corresponding to functional-group composition of the molecule.  $E_{mog}$  given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of alkyl sulfides determined using Eqs. (15.79-15.108) are given in Table 15.158.

s of alkyl sulfides.	Group Symbol	C-S(I)	C-S (ii)	$C - H (CH_3)$	$C - H\left(CH_2\right)$	C.—H	C – C (a)	( <b>,</b> -(; ( <b>b</b> )	ر-ر.(و)	C-C. (q)	(a) .))	(j) .)=.)
Table 15,153. The symbols of functional groups of alkyl sulfides.	Functional Group	C-S (methyl, alkyl)	C-S ((CH ₃ ), C-S-)	CH, group	CH ₂ group	CH	CC bond (n-C)	CC bond (iso-C)	CC bond (tert-C)	CC (iso to iso-C)	CC (t to t-C)	(C) (trin iso-C)

Table 15.1	Fable 15 154. The reometrical bond para	grameters of alkyl sulfides and experimental values [1]	xperimental values	[1].						.,,,,	0
Parameter	C-3 (i)	C - S (ii)	(HJ) H-J	C-H (CH.)	H-J	C-(a)	(a) U-U	(a) U-U	(g) (; -(; (g)	(e) 	E)
		Group	Group	Group	Group	Group	Group	Group	Group	Group	Croup
a (a.)	1.90975	1,90975	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
c. (a)	1.71455	1.71455	1.04856	1.05553	19950:1	1.45744	1.45744	1.45164	1.45744	1,45164	1.45164
Bond Length	1.81460	1.81460	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1,53635
			1.107	1.107			1 523	1 523	1 532	1 532	1 532
Exp. Bond	d 1.807	1.807	H-D)	H-2)	1.122	(propane)	(propane)	(propane)	(propane)	(propane)	(propane)
Length			propane)	propane)	(isobutane)	1.531	1.531	1.531	1.531	1.531	1.531
₹) —-		(ethyl meth	C - H  butane	(C – H butane)		(butane)	(butane)	(butane)	(butane)	(butane)	(butane)
b c (a)	0.84112	0.84112	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
(0)	0 80778	0.89778	0.63580	0,63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Group	2.10725	1.45164	1.53635	1,532 (propane) 1,531 (butane)	1.52750	0.68888
Group	2.10725	1,45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888
Group	2.12499	1,45744	1.54280	(propane) 1.531 (butane)	1,54616	0.68600
Group	2.10725	1.45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888
droup Quonb	2.12499	1.45744	1.54280	1,532 (propane) 1,531 (butane)	1.54616	0.68600
Group	2.12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1,54616	0.68600
Group	1.67465	1.05661	1.11827	1,122 (isobutane)	1.29924	0.63095
$C-H\left(CH_{2}\right)$	1.67122	1.05553	1,11713	1.107 (C-H propane) 1.117 (C-H butane)	1,29569	0.63159
$C-H(CH_3)$	1.64920	1.04856	1.10974	1.107 (C-H propane) 1.117	1.27295	0.63580
C – S (ii) Group	1,90975	1.71455	1.81460	1.807 (dimethyl sulfide) 1.813 (ethyl methyl sulfide, avg.)	0.84112	0.80778
C-S (i) Group	1.90975	1.71455	1.81460	1.807 (dimethyl sulfide) 1.813 (ethyl methyl sulfide, avg.)	0.84112	0.00779
raneter	(0)	(a°)	Bond ength	p. Bond ength (A)	(4)	(0)

Bond	Atom	1,7	E	17	12	Final Total	ļ		E	16.00	,0	•			-
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C2sp³ (eV)	$(a_n)$	$(a_0)$	(eV) Final	(eV) (eV) Final	<u>،</u> (۰	o ( )	( _o )	(a,)	$\begin{pmatrix} a_2 \\ a_4 \end{pmatrix}$
$R-S-R$ ( $(\cdot-S)$ (i) and (ii))	×	-0,36229	-0.36229	0	0		1,32010	0.87495	-15.55033		129,96	50.04	52.88	1.15262	0,56193
$H_1C_a - S - C_bH_2CH_2R$ $(C - S_1(i))$	ڻ	-0.36229	0	0	۵	-151.97798	17716.0	0,89582	-15.18804	-14.99717	130.79	49.21	53.75	1.12957	0.58518
$H_1C_A - S - C_BH_2CH_2R$ (C - S'(i))	ڻ	-0.36229	-0.92918	Û	0	-152.90716	17710.0	811418	-16.11722	-15.92636	128.69	51.31	51.57	1.18689	0.52765
$H_3C_a - S - C_r(CH_3)_3$ (C - S'(i)  and (ii))	ن '	-0.36229	-0.72457	-0.72457	-0.72457	-154.15170	17719.0	0.78367	-17.36176	-17.17090	125.97	54.03	48.94	1,25430	0.46025
('-H (('H')	i.	-0.92918	0	û	0	-152.54487	17716.0	0.86359	-15.75493	-15,56407	77,49	102.51	41.48	1,23564	0.18708
$C - H (CH_2)$	C.	-0.92918	-0.92918	0	0	-153.47406	17716.0	0.81549	-16,68412	-16.49325	68,47	111.53	35.84	1.35486	0.29933
(H (C.H)	j_	-0.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_1^{C}C_{\mu}^{C}H_2^{C}H_2^{-}$ $((C-C^{-}(C)))$	ن	-0.92918	0	0	O	-152,54487	17716.0	0.86359	-15.75493	-15.56407	63.82	116.18	30,08	1.83879	0.38106
$H_1^{\zeta}(L, L, H_2, H_3, L, L, L, L, L, L, L, L, L, L, L, L, L,$	۲,	-0.92918	-0.92918	0	0	-153.47406	17716.0	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R - H_2C_*C_*(H_2C_* - R)HCH_2 - (C - C_*(b))$	۲.	-0.92918	-0.92918	*1676'0-	0	-154,40324	0,9177	0.77247	-17,61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2C_s(R - H_2C_s)C_s(R^{-1} - H_2C_c)CH_2 - (C - C_1C_0)$	۲. ٔ	-0.92918	-0,72457	-0.72457	-0,72457	-154.71860	17716.0	0.75889	-17,92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$ksol'_{s}(\zeta_{s}(H_{2}(\zeta_{s}-R))HCH_{2}-(C-C'(d))$	(;	-0.92918	-0,92918	81626:0-	0	-154.40324	0.91771	0.77247	-17,61330	-17.42244	48.30	131.70	21.90	1.97162	0,51388
$nerC_{\sigma}(R'-H_2C_{\sigma})C_{\sigma}(R''-H_2C_{\sigma})CH_2-$ (( \( -C' \( \epsilon \)))	ڻ	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129,96	22.66	1.94462	0.49298
$urr(C,C,(H_2C_v-R)HCH_2-(C-C'(f))$	۲,	-0,72457	-0.92918	81676 0+	-0	-154,19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$ksaC_{a}(R'-H_{2}C_{a})C_{b}(R''-H_{2}C_{c})C'H_{2} - (C'-C_{c}(f))$	نٔ	-0.72457	-0 72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50,04	129.96	22.66	1.94462	0,49298

Table 15.155. The MO to HO intercept geometrical bond parameters of alkyl sulfides. R, R', R'' are H or alkyl groups.  $E_T$  is  $E_T(anom-anont, msp^1, AO)$ . Bond

Table 15, 156. The energy parameters (eV) of functional groups of airkyl suitides.	ers (ev) or imicul	onal groups of alfy	autiliacs.		11 5	(0)	(J-(, B)	(3) ) - )	(P) U-U	(e) (j-	C-C (f)
Parameters	C 5 (1) Group	C-5 (II) Group	Croum	Group	Group	Group	Group	Group	Group	Group	Group
ı	-	-	3	2		-	1	-			1
1,,		.   c	2	-	, o	0	0	0	0	0	0
"2			1 0	0	C	0	0	0	0	0	0
	> 0	\$0	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
	0.64965	0.64965	-	1	_	1	1	-		-	_
	-	-	-		1	-	-	-	1	1	-
5 ;	-   -	-	0.91771	0.91771	0.91771	0.91771	17716.0	0.91771	0.91771	17716.0	0.91771
27	. 0	0	0	-	-	0	0	0	-	-	0
<u>.</u>	2	2	-		-	2	2	2	2	2	2
27 6	0	0	3	2		0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	5′0	0.5	0.5
:	0 64965	0.64965	-	-		-	-	1	1	-	1
V (eV)	-46,36495	-46.36495	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V (eV)	7.93551	7.93551	38,92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T' (gV)	12 13899	12.13899	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V (eV)	-6.06949	-6,06949	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(10 10) (eV)	0	0	-15.56407	-15.56407	-14.63489	-15,56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
ΔE, 10 (aV)	-0.72457	-0.72457	0	0	0	0	0	0	0	0	0
E. (40 10) (eV)	0.72457	0.72457	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
E_(n.m) (eV)	-31,63537	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{-}(atom - atom, msn^{3}, AO)$ (eV)	-0.72457	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1,44915	-1.44915
$\mathcal{E}_{-1}(w)$ (eV)	-32,35994	-32.35994	-67.69450	-49.66493	-31,63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33,08452
ω (10 ¹⁵ rud/s)	30,5436	8.92777	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9,43699	9,55643	9.55643
(eV)	20.10434	5.87641	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
E (eV)	-0.28705	-0.15519	-0,25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Eknh (eV)	0.08146	0.08146	0.35532	0.35532 (Fa (13.458))	0,35532 (Eq. (13,458))	0.12312	0.17978	0.09944	0.12312	0.12312 [2]	0.12312
Ē (eV)	-0.24632	-0.11446	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803	0,14803	0.14803	0.14803	0.14803
E. Group (eV)	-32.60626	-32.47440	-67,92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E (c, 30 110) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
E 10 10 10 (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{D}(t_{map})$ (eV)	3,33648	3.20462	12.49186	7.83016	3.32601	4.32754	4.29921	3,97398	4.17951	3.62128	3.91734

Table 15.157. The total bond energies of alkyl sulfides calculated using the functional group composition and the energies of Table 15.156 compared to the experimental values [3]. The magnetic energy E_{me} that is subtracted from the weighted sum of the  $E_n(\kappa_{mnp})$  (eV) values based on composition is given by (15.58).

Formula	Formula Name		1170													
	August 1	(=)	(三) (二)	CH.	CH,	E	(; (a)	C-C (P)	(c)	C - C (d) $C - C$ (e)	(c)	C-C (f)	Lz	Calculated	Experimental	Relative Error
		Group	Group								,		You!	Total Bond	Total Bond	
S.H.S	Dimethyl culf.do		•											Energy (eV)	Energy (eV)	
3 .	Cincenty Suniae	4	>	7	ģ	0	0	0	0	0	0	0		31 65668	31 677	0.00048
Cing Cing	Ethyl methyl sultide	-	0	7		0	_	0	c	c	-			47 01430		00000
CHIIS	Diethyl sulfide	6	c	,	,	c		• •				>	>	43.814.18	45.848	0,00078
O.H.	Methyl propert culfide	יו	• •	1 (	4 6	> 0	(	0	9	<b>&gt;</b>	0	0	0	55.97208	56.043	0.00126
17.	frommy propy, service	4 6		4 1	7 (	<b>.</b>	7	0	0	0	0	0	0	55.97208	56.029	0.00102
	Detail mentyl sunde	7 (	>	, ,	0		0	C)	0	0	0	0	0	56.07297	56.115	0.00075
31:50	Duty: memy! suitide	7	5	2	'n	0	~	0	0	0	0	c	c	8702189	68 185	10000
SHO	t-Butyl methyl sulfide	_	_	4	0	c	0	_	,,	-	. <		, •	00.12270	00.100	0.000
S.H.S	Ethyl propyl sulfide	-		,		, ,	•			> 1	>	>	7	68.28245	68.381	0.00144
O.H.	Frhyl isonropyl sulfide	- (	, ,	4 6		> -	٠.	<b>.</b>	0	0	0	0	0	68.12978	68.210	0.00117
, H	Discourant milita	1 6	> 0	o -	7 1		_	2	0	0	0	0	0	68,23067	68.350	0.00174
211111	Donal select antice	4 6	۰ د	4 (	Э.	7	0	4	0		0	0	0	80.48926	80.542	0 00065
21117	Dutyl cullyl suitide	7	0	7	4	0	4	0	0	0	0	0	0	80.28748	80 395	0.00133
2111	Meinyl pentyl sulfide	7	0	7	4	0	4	0	0	0	0	0		80 28748	80 337	0.00056
2 E E	Dibutyl Sulfide	<b>C</b> 1	0	cı	9	0	9	0	0	0	c	•	-	104 60309	107 701	20000
CAHINS	Di-sec-butyl sulfide	7	0	4	2	,	,	•	<			•	٠ د	00700.401	2 4	0.00094
C.H.S	Di-t-butyl suffide	c	,			, <	1 0		> •		>	>	0	104,80466	104.701	-0.00099
H	Dischutyl sulfide		4 6	۰ د	> 0	> (	<b>.</b>	Э,	9	0	0	0	7	104,90822	104.920	0.00011
O.H.	Dinestral cuffide	<b>3</b> (	> 0	<b>†</b> (	7 (	7 (	0 1	9	0	0	0	0	0	104,74800	104.834	0,00082
	Differential sufficient	·) (	۰ د	7 .	×o	P	00	0	0		0	0	o	128,91828	128.979	0.00047
Clarino	Dusopentyl suiting	7	0	4	4	2	7	9	0	0	¢	-	c	120.06240	130 151	00000

					<del></del> -					<del>-</del>					
E.m. O	(o)	99.05 (dimethyl sulfide)	97 (ethyl methyl sulfide)	(ethyl methyl sulfide)	107 (propane)	(propane) 113.8 (butane) 110.8 (isobutane)	111.0 (butane) 111.4 (isobutane)	109.3 (dimethyl suffide) 110 (ethyl methyl sulfide)			110.8 (isobutane)		111.4 (isobutane)	(isobutane)	
0 100	(C)	99.06	97.04	114.27	108.44	110.49	110.49	109.50	109.44	109.44	110.67	110.76	111.27	111.27	107,50
_	© 7a												,		
,	e ©														 
,						69.51	69.51		70.56	70.56					72.50
. Lazar J.	ε _τ (eV)	-1.85836	-1.85836	-0.72457	0		.*	O			-1.85836	G	0	-1.85836	
	v	0.84418	0.83954	0.74282	1.15796			1.15796			0.81549	1.04887	1.04887	1.04887	
1 2 1	<b>5</b> .	-	·	-	0,75			0.75			-	0.75	0.75	0.75	,
Merc Good	ర్'	-	-	0.64965 (Eq. (15.127))	-			-			-	1	-	-	
and angre	Ć	-	1	-	-			-				0.75	0.75	0.75	
ioni inc piece	C2 Atom 2	0:84418	0.81549	0.83600							0.81549	17716.0	0.91771	0.91771	
c parallectors i	ς2 Λtəm ſ	0.84418	0,86359	0,64965 (Eq. (15.127))	0.86359			0.86359			0.81549	0.87495	0.87495	0,87495	
[1]. In the calculation of $\sigma_{\rm t}$ , the parameters from the preceding angle were used.	Atom 2 Hybridization Designation (Table 153 A)	=	25	. 51	н			ж			25	1	1	-	
il, in me ca	E'codombie Atom 2	-16.11722	-16.68412 methylene C,	-16,27490	Œ			H			-16.68412 C	-14.82575 C _b	-14,82575 C _a	-14.82575 C.	
rimental values [	Atom 1 Hybridization Designation	11	7	w	7			7			25	2	\$	35,	
des and expe	E trenfombie Atom I	-16.11722	-15.75493 methyl C,	-10.36001	-15.75493			-15,75493			-16.68412 C _k	-15,55033	-15,55033 C,	-15,55033 C _h	
alkyl suiti	$2c'$ Terminal Atoms $(a_0)$	5.2173	5,1381	5,3364	3,4252			3.4252			4.7958	4.1633	4.1633	4.7958	
ameters of	$\frac{2c'}{\text{Bond } 2}$ ( $a_0$ )	3,42910	3,42910	2.91547	2,11106			2,09711		{	2.91547	2.11323	2.09711	2.90327	
and angle par	2c' Bond I (a ₀ )	3,42910	3.42910	3.42910	2,11106			2.09711			2,91547	2,91547	2.91547	2.90327	
Table 15.158. The bond angle parameters of alkyl sulfides and experimental values	Alonis of Angle	7C,8C,	2C_8C_4 (C - S (i))	ZSC,C,,	Methylene ZHC_H	אנ"נ"נ".	H*.5".)7	Methyl ZHC"H	75"27	H'.5'.37	ZC, C, C, iss	ZC,C,H iso C,	ZC,C,H iso C,	ZC, C, tert C.	,33.37

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DISULFIDES  $(C_n H_{2n+2} S_{2n}, n = 2,3,4,5...\infty)$ 

The alkyl disulfides,  $C_n H_{2n+2} S_{2m}$ , comprise C-S and S-S functional groups. The alkyl portion of the alkyl disulfide may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise 10 functional groups. The branched-chain-alkane groups in disulfides are equivalent to those in branched-chain alkanes.

Each C-S group is equivalent to that of general alkyl sulfides given in the corresponding section. As in the case of thiols and sulifides,  $C_2$  of Eq. (15.52) for the C-S-bond MO given by Eq. (15.127) is  $C_2(C2sp^3HO\ to\ S)=0.64965$  and 15  $E_T(atom-atom, msp^3.AO)$  is  $-0.72457\ eV$  (Eq. (14.151)).

The S-S group is solved as an  $H_2$ -type-ellipsoidal-MO that is energy matched to the energy of sulfur,  $E(S) = -10.36001 \ eV$ , such that  $E(AO/HO) = -10.36001 \ eV$  in Eq. (15.42) with  $E_T(AO/HO) = E(AO/HO)$ . The S-S-bond MO is further energy matched to the  $C2sp^3$  HO of the C-S-bond MO.  $C_2$  of Eq. (15.52) for the S-S-bond MO given by Eq. (15.127) is also  $C_2(C2sp^3HO\ to\ S) = 0.64965$ . In order to match  $E_T(atom-atom,msp^3.AO)$  of the C-S group  $(-0.72457\ eV)$  (Eq. (14.151)),  $E_T(atom-atom,msp^3.AO)$  of the S-S-bond MO is determined using a linear combination of the AOs corresponding to  $-0.72457\ eV$  and  $0\ eV$  in Eq. (15.29), Eq. (15.31), and Eqs. (15.19-15.20). The result corresponding to bond order 1/2I in Table 15.2 is  $E_T(atom-atom,msp^3.AO) = -0.36229\ eV$ .

Table 15.159. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl disulfides are given in Tables 15.160, 15.161, and 15.162, respectively. The total energy of each alkyl disulfide given

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in Table 15.163 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.162 corresponding to functional-group composition of the molecule.  $E_{mag}$  given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of alkyl disulfides determined using Eqs. (15.79-15.108) are given in Table 15.164.

oups of alkyl disulfides. Group Symbol	5-2	S-S	C - H (CH ₃ )	$C-H$ $(CH_2)$	H-J	(; ~ (, (a)	(a) シーン	() しーじ	C-C (d)	() () (e)	(j) 2-2
Table 15.159. The symbols of functional groups of alkyl disulfides. Functional Group Group	C:S	S-S	CH, group	CH ₂ group	CH	CC bond (n-C)	CC bond (iso-C)	CC bond (tert-C)	CC (iso to iso-C)	CC (t to t-C)	CC (t to iso-C)

CC (t to iso-C)	()	(1)	(1								
Table 15.16	Table 15.160. The geometrical bond para:	parameters of alkyl disulfides and experimental values [1].	d experimental valu	es [1].							
Parameter	C S (i) Group	S-S Group	$C-H\left(CH_3\right)$	$C-H(CH_2)$	C~H Group	C - C (a) Group	C-C (b) Group	C-C (e) Group	C-C (d) Group	C-C (e) Group	C-C)
a (a,)	1.90975	2.37173	1,64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.1072
c. (a ₀ )	1,71455	1.91070	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1,4516
Bond Length 2c' (A)	1,81460	2.02220	1.10974	1,11713	1.11827	1.54280	.1.54280	1.53635	1.54280	1.53635	1.5363.
Exp. Bond Length (A)	1.816 (dimethyl disulfide)	2.029 (dimethyl disulfide)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propan 1.531 (butane
b,c (a,)	0.84112	1,40510	1.27295	1.29569	1,29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.5275
	0.89778	0.80562	0.63580	0.63159	0.63095	0.68600	0.68600	88889'0	0.68600	0.68888	0.6888

Bond	Atom					F									
		r. ;		E _T	£,	rinal lotal	fathal	final	Erratous	$E(C2sp^3)$	.θ	Φ.	θ,	ď,	ď,
		(ev) Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	(72 <i>p</i> )	(a _o )	(a _a )	(eV) Final	(eV) Final	©	<u>(</u> )	•	(%)	$(a_a)$
RS-SR (C-S (i) and (ii))	×	-0.36229	-0.18114	0	0		1.32010	0.88527	-15.36918		94.25	85.75	38.93	1.84513	0.06558
$H_3C_{\mu} - SS - C_{\mu}H_2CH_2R$	ن	-0,36229	O	0	0	-151.97798	17716.0	0.89582	-15.18804	-14.99717	130.79	49.21	53.75	1.12937	0.58518
$H_3C_a - SS - C_bH_2CH_2R$ $(C - S_3)$	۲,	-0.36229	-0.92918	0	0	-152.90716	17716.0	0.84418	-16.11722	-15.92636	128.69	51.31	51.57	1,18689	0.52765
	ڻن	-0.36229	-0.72457	-0.72457	-0.72457	-154.15170	17716.0	0.78367	-17.36176	-17.17090	125.97	54.03	70 87	1.35/30	20002
('-H (CH;)		-0.92918	0	0 .	0	-152.54487	17716.0	0.86359	-15.75493	-15.56407	77.49	102.51	41,48	1,23564	0.18708
$C - H \left( CH_3 \right)$	۲.	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	135486	52006.0
(H (cH)	C	-0.92918	-0.92918	-0.92918	D	-154,40324	0.91771	0,77247	-17.61330	-17,42244	61.10	118.90	31.37	1 42988	702420
$H_3C_c H_2CH_2 - (C - C, (a))$	".	-0.92918	0	С		-152.54487	17710	0.86359	-15.73493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_{\hat{s}}C_{s}H_{\hat{s}}CH_{\hat{s}} (C-C_{s}G_{s})$	۲.)	-0.92918	-0.92918	0	0	-153,47406	17716.0	0.81549	-16.68412	-16.49325	36.41	123.59	26.06	1.90890	0.45117
$R - H_2 C_a C_b \Big( H_2 C_c - R^2 \Big) H C H_2 - \Big( C - C \cdot (b) \Big)$	ر.'	-0.92918	-0.92918	-0.92918	0	-154,40324	17716.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2 C_o(R' - H_2 C_o) C_b(R'' - H_2 C_o) C H_2 - (C' - C'(\phi))$	C,	-0.92918	-0.72457	-0.72457	-0 72457	-154.71860	17716.0	0.75889	-17.92866	-[7.73779	48.21	131.79	21.74	1.95734	0.50570
$ixoC_{i}C_{k}(H_{2}C_{i}-R_{i})HCH_{2}-(C-C_{i}(d))$	C,	-0.92918	-0.92918	-0.92918	0	-154,40324	12216.0	0.77247	-17.61330	-17.42244	48.30	131,70	21.90	1.97162	0.51388
$ler(C_{\alpha}(R-H_{2}C_{d})C_{b}(R^{n}-H_{2}C_{c})CH_{2}-(C-C_{\alpha}(e))$	G,	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$ler(C_{\mathcal{L}}(H_{2}C_{\epsilon}-R)HCH_{2}-(C-C_{\epsilon}(f))$	ڻ	-0.72457	-0.92918	-0.92918		-154.19863	17716.0	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$lsoC_{\sigma}(R'-H_2C_{\sigma})C_{\delta}(R''-H_2C_{\sigma})CH_2-$ (C'-C' (f))	ڻ	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.76763	-17.92866	-17.73779	50.04	129.96	22.66	1,94462	0.49298

Table 15.161. The MO to HO intercept geometrical bond parameters of alkyl disulfides. R, R', R' are H or alkyl groups.  $E_T$  is  $F_T$  (atom — atom,  $msp^2$  AO). Bond Rond  $E_T$  is  $F_T$  Final Total  $F_T$ 

	Group	Group	('H ₃ Group	C'H ₂ Group	C → H Group	C – C (a) Group	C-C (b) Group	(c) Group	C-C (d) Group	C – C (e) Group	C-C (f) Group
	_		3	2	-	_	-	_	_	-	-
n,	0	0	2	-	0	0	٥	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	2,0
	0.64965	0.64965	-	-	1	_	-	_	_		-
	1	-	-	_	1	_	-	1	1	-	-
	_		0,91771	0.91771	0.91771	0.91771	0.91771	0,91771	0.91771	0.91771	17716.0
	0	0	0		1	0	0	0		-	0
	2	2		-	-	2	2	2	2	2	2
	0	0	'n	2	1	0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
	0.64965	0.64965	1	1		_	1		-	-	_
V, (eV)	-46,36495	-31.74215	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	7.93551	7.12083	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	12,13899	6.69177	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V (cV)	-6.06949	-3.34589	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
El.w no) (cV)	0	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-15,35946
$\Delta E_{n,sto}(\infty no)$ (eV)	-0.72457	0	0	0	0	0	0	0	0	0	0
Er (.10 110) (eV)	0.72457	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(n_1, n_0)$ (eV)	-31.63537	-31.63544	-67.69451	-49.66493	-31,63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom - atom, msp^3.AO)$ (cV)	-0.72457	-0.36229	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
E _T (sw) (eV)	-32.35994	-31.99766	-67.69450	-49,66493	-31.63537	-33.49373	-33.49373	-33.08452	-33,49373	-33.08452	-33.08452
$\omega \left(10^{15} rad/s\right)$	30.5436	6.45076	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9,55643	9.55643
$\vec{E}_{\mathrm{K}}$ (eV)	20,10434	4.24600	16.40846	15.97831	15,91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\vec{E}_{\mu}$ (eV)	-0.28705	-0.13044	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
(eV)	0.08146	0.06745 N	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978	0.09944	0.12312	0.12312	0.12312
$\vec{E}_{us}$ (eV)	-0.24632	-0.09672	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{mog}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Er (Grage) (eV)	-32.60626	-32.09437	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E mand (c, 30.110) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
E metel (4. 10 110) (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
E. (Grave) (eV)	227740										

Table 15.163. The total bond energies of alkyl disulfides calculated using the functional group composition and the energies of Table 15.162 compared to the experimental values [3]. The magnetic energy E equation is subtracted from the weighted sum of the

	֡														
Formula	Name	C~S Group	S-S Group	(.H ₃	CH,	HD	( - ( (a)	C-C (b)	(0) 2-2	C-C (d)	(e) 2-2	C-C (t)	ĮĮ.	Calculated Total Bond	Experimental Total Bond
SH'S	Dintellation distributed	3	-						-					Energy (eV)	Energy (eV)
500		4 1		7	>	0	•	>	-	0	0	0	0	34.48127	34413
ž Ž	Diethyl distillide	7	_	2	7	0	7	0	c	c	_	-	•	20 70.67	2007
Ę.	Dinronyl disulfide	,	-	·	c			. ;		0 1	•	•	•	20,7300	26.8/3
	and the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of t	1	-	4	2	<b>+</b>	4	=	0	0	0	0	0	83 11207	83 169
CALINA	Di-t-buty! disulfide	7		9	c	=	_	c	٠	c	•		, (	0000000	

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103689 S S C _a 14.8237 16.6841 16.6841 (c) (c) (c) (c) (c) (c) (c) (c)
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- 14.82377 
16.6841 16.6841 17
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H H H
-16,6841 - C. -14,8257 -14,8257
-16.6841 - C; -14.8257 -14.8255
-16.6841 - C; -14.8257 -14.8257
-(4.825) -(°, -14.825) (°,
-14,8257
-14.82575
-

SULFOXIDES 
$$(C_n H_{2n+2}(SO)_m, n = 2,3,4,5...\infty)$$

The alkyl sulfoxides,  $C_n H_{2n+2}(SO)_m$ , comprise a C-SO-C moiety that comprises C-S and SO functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  3P_2 . The SO functional group comprises a double bond between the two unpaired electrons of O. The sulfur 15 atom is energy matched to the  $C2sp^3$  HO. In alkyl sulfoxides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the S AO has an initial energy of  $E(S) = -10.36001 \, eV$  [38]. To meet the equipotential condition of the union of the  $S = O H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the S = O-bond MO given by Eqs. (15.68) and (15.70) is

$$c_{2}(O \text{ to } S3sp^{3} \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(S)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}}(0.91771)$$

$$= 1.20632$$
(15.128)

The S atom also forms a single bond with each of the  $C2sp^3$  HOs of the two C-S groups. The formation of these bonds is permitted by the hybridization of the four electrons of the S3p shell to give the orbital arrangement:

25

where the quantum numbers  $(\ell, m_{\ell})$  are below each electron. The 3s shell remains unchanged. Then, the Coulombic energy  $E_{Coulomb}(S, 3sp^3)$  of the outer electron of the  $S3sp^3$  shell given by Eq. (15.118) with  $r_{3sp^3} = 1.17585a_0$  (Eq. (15.119)) is -11.57099~eV. Using Eq. (15.16) with the radius of the sulfur atom  $r_{16} = 1.32010a_0$  given by Eq. (10.341), the energy  $E(S3sp^3)$  of the outer electron of the  $S3sp^3$  shell is given by the sum of  $E_{Coulomb}(S3sp^3)$  and E(magnetic):

$$E(S3sp^{3}) = \frac{-e^{2}}{8\pi\epsilon_{0}r_{3,p^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}r_{16}^{3}}$$

$$= \frac{-e^{2}}{8\pi\epsilon_{0}1.17585a_{0}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}(1.32010a_{0})^{3}}$$

$$= -11.57099 \ eV + 0.04973$$

$$= -11.52126 \ eV$$
(15.130)

Then, the hybridization energy  $E_{hyhridization}(S3sp^3)$  of the  $S3sp^3$  HO is

$$E_{hybridization}(S3sp^{3}) = E(S3sp^{3}) - E(S)$$

$$= -11.52126 \ eV - 10.36001 \ eV$$

$$= -1.16125 \ eV$$
(15.131)

The SO group is matched to the C-S group with which it shares the common 10 hybridized S atom. Consequently,  $E_{hybridization}\left(S3sp^3\right)$  is subtracted from  $E_T\left(Group\right)$  in the determination of  $E_D\left(Group\right)$  (Eq. 15.56)). Furthermore, the energy of the S=O-bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with the energy matched to the final energy of the hybridized S atom such that  $E\left(AO/HO\right)=E\left(S3sp^3\right)=-11.52126\ eV$  a n d 15  $\Delta E_{H_2MO}\left(AO/HO\right)=E_{hybridization}\left(S3sp^3\right)=-1.16125\ eV$ . Then,  $E_T\left(AO/HO\right)=E\left(S\right)=-10.36001\ eV$ . Also,  $E_T\left(atom-atom,msp^3.AO\right)$  of the S=O bond is zero since there are no bonds with a  $C2sp^3$  HO.

The C-S group is solved as an energy minimum by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell and by hybridizing the four S3p electrons to form a  $S3sp^3$  shell, and the sharing of electrons between the  $C2sp^3$  HO and the  $S3sp^3$  HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic

energy of the  $S3sp^3$  shell,  $E_{Coulomb}\left(S3sp^3\right)$  given by Eq. (15.120) in Eq. (15.63), the  $S3sp^3$ -shell hybridization factor,  $c_2\left(S3sp^3\right)$ , is

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \ eV}{-13.60580 \ eV} = 0.85045$$
 (15.132)

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the 5 Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus,  $c_1$  and  $c_2$  are equal to one in Eq. (15.52), and the energy matching condition is determined by the  $C_2$  parameter. In alkyl sulfoxides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)) and the  $S3sp^3$  HO has an energy of  $E(S3sp^3) = -11.52126 \, eV$  (Eq. (15.130)). To meet the equipotential condition of the union of the C-S  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.52) for the C-S-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ S3sp^3\right) = \frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)}c_2\left(S3sp^3\right) = \frac{-11.52126\ eV}{-14.63489\ eV}\left(0.85045\right) = 0.66951\ \ (15.133)$$

As in the case of thiols, sulfides, and disulfides, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the C-S-bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with  $E(AO/HO) = 0 \qquad \text{and} \qquad E_T \left( AO/HO \right) = \Delta E_{H_2MO} \left( AO/HO \right). \qquad \text{For sulfoxides,}$   $\Delta E_{H_2MO} \left( AO/HO \right) = -0.72457 \ eV \ . \qquad \qquad \text{Further equivalently,}$   $E_T \left( atom-atom, msp^3.AO \right) = -0.72457 \ eV \ (\text{Eq. (14.151)}).$ 

The symbols of the functional groups of branched-chain alkyl sulfoxides are given in Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfoxides are given in Tables 15.166, 15.167, and 15.168, respectively. Consider that the C-S bond is along the x axis in the xy-plane. The S nucleus is at the focus +c and the C nucleus is at the focus -c. The elliptic angle  $\theta'$  is taken as counterclockwise from the x-axis for S and as clockwise from the -x-axis for C. The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.168 corresponding to functional-

group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.79-15.108) are given in Table 15.170.

Table 15.165. The symbols of functional groups of alkyl sulfoxides.

Functional Group	Group Symbol
C-S	C-S
SO	SO
CH₃ group	$C-H$ $\left(CH_{_{3}}\right)$
CH₂ group	$C-H$ $\left(CH_{2}\right)$
СН	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Parameter C S	S=3	OS	(HJ) H)	(HJ) HTJ		C~C (a)	(a) )-)	(e) D-D	(g)	(G) (C-(C)	(E)
	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
a (a ₀ )	1.87325	1.98517	1.64920	1,67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
(g)	1.67271	1.40896	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2c' (A)	1.77031	1,49118	1.10974	1.11713	1,11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (A)	l. 799 (dimethył sulfoxide)	1,485 (dimethyl sulfoxide)	1.107 (C - H propane) 1.117 (C - H butane)	L.107 (C-H propane) L.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	L.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
b,c (a)	0.84328	1,39847	1,27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
	0.80204	A 7007 0	0.63580	051590	0 63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

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Table 15.167. The MO to HO intercept geometrical bond parameters of alkyl sultoxides. $R,R',R''$ are $H$ or alkyl groups. $L_T$ is $L_T$ alon $L_T$ alon, $R_T$ and $R_T$ are $R$ or alkyl groups. $L_T$ is $L_T$ alon $L_T$ and $R$	netrical bon	d parameters of	alkyl suffoxides.	. K.K.K. are I	7 or ankys group	35. L _T 15 L _T (a)	וסווו – מוסווו, חוגוַ	P.AO).		i					
Bond	Atom	E	E	E,	E,	Final Total	, estat	1	Economb	$E(C2sp^3)$	ι,θ	θ	θ,	ď	d ₂
		(eV) Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C2sp³	$(a_0)$	$(a_0)$	(eV) Final	(eV) Final	©	©	<u></u>	(a ₀ )	(a ₀ )
R.S=0	×	0	-0.36229	-0.36229	0	(eV)	1,32010	0.87495	-15.55033		79.78	100.22	38.00	1.56425	0.15529
R.S = 0	0	D	٥	0	0		1.00000	0.91771	-14.82575		84.06	95.94	40.75	1,50400	0.09504
R, -50	S.	-0.36229	-0.36229	0	0		1,32010	0.87495	-15.55033		129.35	50.65	53.36	1.11799	0.55472
H,C, -5(0) - C,H,CH,R	ڻ	-0,36229	Q	0	0	-151.97798	17716.0	0.89582	-15.18804	-14.99717	130.19	49.81	54.24	1.09461	0,57809
H3C,-S(O)-C,H2CH2R	C,	-0.36229	-0.92918	0	0	-152,90716	17716.0	0.84418	-16.11722	-15.92636	128,05	51.95	52.03	1.15245	0.52026
$C-H$ $(CH_3)$	ŭ	-0,92918	0	0	0	-152.54487	17719.0	0.86359	-15.75493	-15,56407	77.49	102,51	41.48	1.23564	0.18708
$C-H$ $(CH_2)$	ر	81626'0-	-0.92918	0	0	-153.47406	12216.0	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
C-H (CH)	J	-0.92918	-0.92918	-0.92918	0	-154.40324	17716.0	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_1C_1C_1H_2CH_2$ —(C-C (a))	ບໍ	-0.92918	0	ø	0	-152,54487	17716,0	0,86359	-15.75493	-15,56407	63.82	116.18	30.08	1.83879	0.38106
$H_1C_0C_1H_2CH_2$ – $(C-C'(a))$	ű	-0.92918	-0.92918	0	0	-153,47406	17716.0	0,81549	-16.68412	-16.49325	36,41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_b-R)HCH_2 C=C_b(h)$	౮	-0.92918	-0.92918	-0.92918	. 0	-154,40324	0,91771	0.77247	-17.61330	-17,42244	48.30	131.70	21.90	1.97162	0,51388
$R - H_2C_a(R' - H_2C_a)C_b(R'' - H_2C_b)C'H_2 - (C - C_1(G))$	ڻ '	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	17716.0	0,75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$ixoC_{\alpha}C_{\alpha}(H_{\alpha}C_{\alpha}-R^{2})HCH_{\alpha}-(C-C^{2})$	ڻ	-0.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$len(C_a(R^* - H_2C_a)C_b(R^* - H_2C_c)CH_2 - (C - C^*(e))$	ڻ	-0,72457	-0.72457	-0.72457	-0.72457	-154.51399	177100	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$ler(C_n(H_2C_n - R^n)HCH_2 - (C - C^n(f))$	υ*	-0.72457	-0.92918	-0.92918	Û.	-154.19863	17716.0	0.78155	-17.40869	-17.21783	52.78	127,22	24.04	1,92443	0,47279
$isoC_{u}(R'-H_{2}C_{s})C_{k}(R''-H_{2}C_{c})CH_{2}-$	ڻ	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1,94462	0.49298

I able 13, 168. The energy parameters (e.v.) of full citoting groups of anyl surrovines.	TS (C v ) Or immen	July Proups of air,	sautovines.								
Parameters	C-S	So	(.H.)	Æ,	Ground Ground	Groun	(p)	(c) (c) Group	(a) Croup	(a) Cloud Group	Group
	Croup	cronb	Group	Group	Group	diodio	dronb	discip	dans	,	
'n	_	7	'n	2	1	1	-	-		1	-
12,	0	0	2	1	0	0	0	0	0	0	0
11.	0	0	0	0	0	0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0,5	0.5	0.5	0.5
	0,66951	_	_	-	-	-	-1		1	1	1
e.	-		_	_	-	_	-	1	1	1	-
6.	_	1.20632	0.91771	0.91771	0.91771	0.91771	0.91771	17710.0	0.91771	0.91771	0,91771
<i>c.</i>	0	0	0	_	-	0	0	0		1	0
¢,	2	4	_			2	2	2	2	2	2
2	0	-	3	2	-	0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	0.5	6.5	6.5	0.5	0.5
.)	0,66951	-	-	_	-	-	_	1		1	
V_ (eV)	-46.73032	-82.63003	-107,32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_ (eV)	8.13401	19,31325	38.92728	25.78002	12.87680	9,33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	12.47306	20.81183	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V (eV)	-6.23653	-10.40592	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3,45250
E(.so na) (eV)	0	-11.52126	-15,56407	-15,56407	-14.63489	-15,56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
ΔΕ _{H,310} (40 110) (eV)	-0.72457	-1.16125	0	0	0	0	0	0	0	0	
$E_{\tau}(\text{no no})$ (eV)	0.72457	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15,56407	-15,35946	-15,35946
Erlusmo (eV)	-31.63521	-63.27088	-67.69451	-49,66493	-31,63533	-31,63537	-31.63537	-31,63535	-31,63537	-31,63535	-31.63535
$E_{\tau}(atom - atom, msp^3, AO)$ (eV)	-0.72457	0	0	0	0	-1.85836	-1.85836	-1,44915	-1.85836	-1.44915	-1.44915
E. (110) (eV)	-32,35994	-63.27074	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33,49373	-33.08452	-33.08452
a (1015 rad 1.5)	30.8880	17.6762	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9,55643
E. (eV)	20.33104	11.63476	16.40846	15.97831	15.91299	6.21159	6:21159	10.19220	6.21159	6.29021	6.29021
Ē, (eV)	-0.28866	-0.21348	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{\mathcal{E}}_{\mathrm{Koh}}\left(eV ight)$	0.08543	0.12832	0,35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 f2l	0.17978	0.09944 [5]	0.12312 [2]	0.12312	0.12312 [2]
E_ (eV)	-0,24595	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Energy (eV)	0.14803	0.11441	0.14803	0,14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\tau}(inop)$ (eV)	-32.60589	-63.56937	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33,18712	-33,18712
E (c. 10 110) (eV)	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489
E money (c, 40 110) (eV)	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
E., (any) (eV)	3.33611	3.86856	12.49186	7.83016	3.32601	4,32754	4.29921	3.97398	4.17951	3.62128	3.91734

C-C(f) Table 15.169. The total bond energies of alkyl sulfoxides calculated using the functional group composition and the energies of Table 15.168 compared to the experimental values [3].

Formula Name C-S SO  $CH_3$   $CH_4$  C-C (a) C-C (b) C-C (c) C-C (d) C-C (e) C-C (e)

	Exp. <i>\theta</i>	96.6 (dimethyl sulfoside	106.7 (dimethy† sulfoxide	107 (propane)	f f2 (propane) 13,8 (butane) 110,8 (isobutane)	111.0 (butane) 111.4 (isobutane)	110.3 (dimethyl sulfoxide			110.8 (isobutane)		(111.4 (fsobutane)	111.4 (isobutane)	
	(cal. 0	96.20	106.88	108.44	110.49	110.49	109.50	109.44	109.44	110.67	110.76	111.27	72111	107.50
	(e)													
Ì	(3)													
	(e)				69.51	69,51		70,56	70.56					72,30
sp. AU).	E, (eV)	-1.85836	-1.65376	ø			0			-1.85856	0	0	-1.85836	
m – alom, m	٠ و	0.82562	0.87489	1.15796			1.15796			0.81549	1.04887	1.04887	1.04887	
7 15 ET (010	5	-	-	0,75		, i	0.75			-	0.75	0.75	0.75	
ere used.	υ _ν		-	_			1			-	ı	~	1	
ing angle w	ن	-		1			-			-	0.75	0.75	0.75	
om the preced	C ₂ Atom 2	0.82562	0.85395 (Eq. (15.114))	_			-			0.81549	17718	0.91771	0.91771	
parameters fi	C ₂	0.82562	0.89582	0.86359			0,86359			0.81549	0.87495	0.87495	0.87495	
culation of $\theta_r$ , the	Atom 2 Hybridization Designation (Table 15.3.4)	21	0	н			æ			25	_	1	_	
i]. In the ca	E couperke Alom 2	-16.47951	-13.61806 O	=			æ			-16,68412 C	-14.82575 C,	-14,82575 ('a	-14.82575 C.	
erimental values [	Atom I Hybridization Designation (Table 15.3.4)	21	7	7			1			52	יאי	מו	5	
ides and exp	E Cadonine Alora 1	-16.47951	-15.18804 C.	-15.75493			-15.75493			-16.68412 (',	-15.55033	-15.33033	-15.55033	
alkyi sulfox	2c' Terninal Atons (a _a )	4,9800	4,959X	3,4252			3,4252			4.7958	4,1633	4,1633	4,7958	
rameters of	2c' Bond 2 (a _p )	3,34541	281792	2,11106			2,09711			2,91547	2.11323	2.09711	2,90327	
and angle pa	2c' Bend 1 (a ₀ )	3,34541	3,34541	2,11106			2,09711			2.91547	2.91347	2.91547	2.90327	
Table 15.170. The bond angle parameters of alkyl sulfoxides and experimental values [1]. In the calculation of 0, the parameters from the preceding angle were used. L, 1s L, (drom - drom, thip Al.)	Alonn of Angle	,x, ,7Z	75,37	Methylene ZHC "H	יאנ"נ"ל.	H3537	Halin I	۷.۵٬۵۲	H", J, J, Z	ای ور" در"ر" در"	") test	") "! H" J" J7	امر ر " 7ر از "ر "	70.007

SULFOXIDES 
$$(C_n H_{2n+2}(SO)_m, n = 2,3,4,5...\infty)$$

The alkyl sulfoxides,  $C_nH_{2n+2}(SO)_m$ , comprise a C-SO-C moiety that comprises C-S and SO functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2CH)$  and t-butyl  $((CH_3)_3C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl (C-C) bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^22s^22p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  3P_2 . The SO functional group comprises a double bond between the two unpaired electrons of O. The sulfur 15 atom is energy matched to the  $C2sp^3$  HO. In alkyl sulfoxides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the S AO has an initial energy of  $E(S) = -10.36001 \, eV$  [38]. To meet the equipotential condition of the union of the S = O H₂-type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the S = O-bond MO given by Eqs. (15.68) and (15.70) is

$$c_{2}(O \text{ to } S3sp^{3} \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(S)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}}(0.91771)$$

$$= 1.20632$$
(15.128)

The S atom also forms a single bond with each of the  $C2sp^3$  HOs of the two C-S groups. The formation of these bonds is permitted by the hybridization of the four electrons of the S3p shell to give the orbital arrangement:

$$\frac{3 \text{sp}^3 \text{ state}}{1,-1} \quad \frac{\uparrow}{1,0} \quad \frac{\uparrow}{1,1} \tag{15.129}$$

25

where the quantum numbers  $(\ell, m_{\ell})$  are below each electron. The 3s shell remains unchanged. Then, the Coulombic energy  $E_{Coulomb}(S, 3sp^3)$  of the outer electron of the  $S3sp^3$  shell given by Eq. (15.118) with  $r_{3sp^3} = 1.17585a_0$  (Eq. (15.119)) is -11.57099~eV. Using Eq. (15.16) with the radius of the sulfur atom  $r_{16} = 1.32010a_0$  given by Eq. (10.341), the energy  $E(S3sp^3)$  of the outer electron of the  $S3sp^3$  shell is given by the sum of  $E_{Coulomb}(S3sp^3)$  and E(magnetic):

$$E(S3sp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{3sp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}r_{16}^{3}}$$

$$= \frac{-e^{2}}{8\pi\varepsilon_{0}1.17585a_{0}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}\left(1.32010a_{0}\right)^{3}}$$

$$= -11.57099 \ eV + 0.04973$$

$$= -11.52126 \ eV$$
(15.130)

Then, the hybridization energy  $E_{hyhridization}(S3sp^3)$  of the  $S3sp^3$  HO is

$$E_{hybridization}(S3sp^{3}) = E(S3sp^{3}) - E(S)$$

$$= -11.52126 \ eV - 10.36001 \ eV$$

$$= -1.16125 \ eV$$
(15.131)

The SO group is matched to the C-S group with which it shares the common 10 hybridized S atom. Consequently,  $E_{hybridization}\left(S3sp^3\right)$  is subtracted from  $E_T\left(Group\right)$  in the determination of  $E_D\left(Group\right)$  (Eq. 15.56)). Furthermore, the energy of the S=O-bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with the energy matched to the final energy of the hybridized S atom such that  $E\left(AO/HO\right)=E\left(S3sp^3\right)=-11.52126\ eV$  a n d 15  $\Delta E_{H_2MO}\left(AO/HO\right)=E_{hybridization}\left(S3sp^3\right)=-1.16125\ eV$ . Then,  $E_T\left(AO/HO\right)=E\left(S\right)=-10.36001\ eV$ . Also,  $E_T\left(atom-atom,msp^3.AO\right)$  of the S=O bond is zero since there are no bonds with a  $C2sp^3$  HO.

The C-S group is solved as an energy minimum by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell and by hybridizing the four S3p electrons to form a  $S3sp^3$  shell, and the sharing of electrons between the  $C2sp^3$  HO and the  $S3sp^3$  HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic

energy of the  $S3sp^3$  shell,  $E_{Coulomb}(S3sp^3)$  given by Eq. (15.120) in Eq. (15.63), the  $S3sp^3$ -shell hybridization factor,  $c_2(S3sp^3)$ , is

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \ eV}{-13.60580 \ eV} = 0.85045$$
 (15.132)

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the 5 Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus,  $c_1$  and  $c_2$  are equal to one in Eq. (15.52), and the energy matching condition is determined by the  $C_2$  parameter. In alkyl sulfoxides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)) and the  $S3sp^3$  HO has an energy of  $E(S3sp^3) = -11.52126 \, eV$  (Eq. (15.130)). To meet the equipotential condition of the union of the C-S  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.52) for the C-S-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ S3sp^3\right) = \frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)}c_2\left(S3sp^3\right) = \frac{-11.52126\ eV}{-14.63489\ eV}(0.85045) = 0.66951\ \ (15.133)$$

As in the case of thiols, sulfides, and disulfides, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the C-S-bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with  $E(AO/HO) = 0 \qquad \text{and} \qquad E_T \left( AO/HO \right) = \Delta E_{H_2MO} \left( AO/HO \right). \qquad \text{For sulfoxides,}$   $\Delta E_{H_2MO} \left( AO/HO \right) = -0.72457 \ eV \ . \qquad \qquad \text{Further equivalently,}$   $E_T \left( atom-atom, msp^3.AO \right) = -0.72457 \ eV \ (\text{Eq. (14.151)}).$ 

The symbols of the functional groups of branched-chain alkyl sulfoxides are given in Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfoxides are given in Tables 15.166, 15.167, and 15.168, respectively. Consider that the C-S bond is along the x axis in the xy-plane. The S nucleus is at the focus +c and the C nucleus is at the focus -c. The elliptic angle θ' is taken as counterclockwise from the x-axis for S and as clockwise from the -x-axis for C. The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as the sum over the integer multiple of each E_D (Group) of Table 15.168 corresponding to functional-

group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.79-15.108) are given in Table 15.170.

Table 15.165. The symbols of functional groups of alkyl sulfoxides.

Functional Group	Group Symbol
C-S	C-S
SO	SO
CH₃ group	$C-H$ $\left( CH_{_{3}}\right)$
CH ₂ group	$C-H$ $\left( CH_{2}\right)$
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	
CC (t to iso-C)	C-C (f)

C - H (CH ₂ )   C - H (CH ₂ )   C - H   C - C (a)	ر - ر ر	S	( )	1		27.0					
1.98517   1.64920   1.67122   1.67465   2.12499   2.10725   2.12499   2.10725   2.10725     1.40866   1.04856   1.05553   1.05661   1.45744   1.45164   1.45164   1.45164   1.45164     1.49118   1.10974   1.1173   1.11827   1.54280   1.54280   1.53635   1.53635   1.53635     1.485   (C-H (C-H (C-H (C-H (C-H (C-H (C-H (C-H	dn	Group	$C = H \left( CH_3 \right)$ Gream	Groun	Group	Group	C-C (b) Group	C-C (c) Group	C - C (d) Group	C-C (e) Group	C-C (f) Group
1,40896   1,04836   1,05553   1,05661   1,45744   1,45744   1,45164   1,45744   1,45164   1,45164   1,45164   1,45164   1,45164   1,45164   1,45164   1,45164   1,45164   1,45164   1,45164   1,45164   1,45164   1,45164   1,45164   1,45164   1,45164   1,45164   1,45164   1,45164   1,532   1,532   1,532   1,532   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,531   1,53	7325	1.98517	1.64920	1.67122	-	2.12499	2 12499	2 10725		3 10201	1
1.49118	177	1 40896	1 04056	1,0000	. 02.00			2:10/22	7.12433	7.107.2	27,01.7
1.49118   1.10974   1.11713   1.11827   1.54280   1.54280   1.53635   1.54280   1.53635   1.54280   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.536355   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.53635   1.536355   1.536355   1.536355   1.536355   1.536355   1.536355   1.536355   1.536355   1.536355   1.536355   1.536355   1.536355   1		0,000	1.04030	1,05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
1.485   C - H   C - H   L.122   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cropane   Cr	)31	1.49118	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
1.485   (C-H   (C-H   1.122   1.532   1.532   1.532   1.532   1.532   1.532   1.532   1.532   1.532   1.532   1.532   1.532   1.532   1.532   1.532   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531   1.531			1.107	1.107		1 633	000				
(Girnethy) Sulfoxide) (L117 (Isobutane) 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.531 1.	99		(C-H propage)	(C-H	1.122	(propane)	(propane)	(propane)	(propane)	1.532 (propane)	1.532 (nronane)
(C-H butane)         (C-H butane)         (Dutane)	moxide)		1,117	1,117	(isobutane)	1.531	1.531	1.531	1.531	1.531	1.531
1.39847         1.27295         1.29264         1.24616         1.34616         1.54550         1.54616         1.54616         1.54616         1.54616         1.54616         1.52750         1.54616         1.52750           0.70974         0.63580         0.63505         0.68600         0.68600         0.68888         0.68200         0.68800			(C-H) butane)	(C-H  butane)		(putane)	(butane)	(butane)	(butane)	(butane)	(butane)
0.70974 0.63580 0.63159 0.63095 0.68600 0.68600 0.68888 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.686000 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.68600 0.686	328	1.39847	1.27295	1,29569	1.29924	1.54616	1.54616	1.52750	1,54616	1.52750	1 52750
	294	0.70974	0.63580	0.63159	0.63095	0.68600	0.68600	0 68888	0 68600	888890	000000

Table 15.166. The geometrical bond parameters of alkyl sulfoxides and experimental values [1].

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		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C2sp ³	(00)	(a ₀ )	(eV)	(eV)	<b>©</b>	- ①	(0.7	(a, 1)	(a')	
0						(e,				Final					-	
$R_i S = O$	s	0	-0.36229	-0.36229	0		1,32010	0.87495	-15.55033		70 78	100.22	20.00	201721		
$R_iS = O$	0	0	o	0	0		1 00000	1771	525C8 PT		010	100.22	38.00	1.36423	0.15529	
R, SO	s	-0.36229	-0.36229	0	0		1 37010	0 87405	C1 C20.71-		94.00	75.74	40.75	1.50400	0.09504	
$H_3C_a - S(O) - C_bH_2CH_2R$	ڼ	-0.36229	0	0	0	-151.97798	122160	0.80587	-15 1880A	7170011	55.62	50.65	53.36	1.11799	0.55472	
$H_3C_a - S(O) - C_bH_2CH_2R$	ڻ	-0,36229	-0.92918	0	0	-152.90716	12210	0.84418	.16 1177	71765-1-	170 051	49.81	42.42	1.09461	0.57809	
$C - H$ $(CH_3)$	٤	-0.92918	0	0	0	-152.54487	17716.0	0.86359	.15 75493	-15 56407	CV.021	26.10	50.75	47777	0.52026	
r - H (CH ₂ )	C	-0.92918	-0.92918	0	0	-153.47406	12210	0 81549	-16 68417	16 40205	25.00	15,201	41.40	1.23304	0.18708	
л – H (CH)	į	-0.92918	-0.92918	-0,92918	0	-154 40324	0.01771	Thoras a	0001741	CARCETON TO	00.47	ecili.	35.84	1,35486	0.29933	
H.C.C.H.CH. –								0.11241	UCC10.71-	+677471-	61.10	118.90	31.37	1.42988	0.37326	
C - C(a)	υ"	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106	
$H_3^{\zeta}C_gC_gH_2^{\zeta}CH_2^{\zeta}-C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta}C_{\zeta}^{\zeta$	౮	-0,92918	-0.92918	0	0	-153,47406	17716.0	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117	
$R = H_2C_aC_b(H_2C_c - R^c)HCH_2 - C - C(b)$	ซ์	-0.92918	-0.92918	-0.92918	0	-154,40324	0,91771	0.77247	-17.61330	-17.42244	48,30	131.70	21.90	1.97162	0.51388	
$(-H_2C_a(R'-H_2C_a)C_b(R''-H_2C_c)CH_2-C_c)$	ڻ*	-0.92918	-0.72457	-0.72457	-0.72457	-154,71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	27.17	P 05724	0.50570	
$voC_sC_k(H_2C_s-R^s)HCH_2-C_sC_sC_s(d))$	บ้	-0.92918	-0.92918	-0.92918	0	-154.40324	17716.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	197162	0.5138.8	
$2\pi C_s(R'-H_2C_s)C_s(R''-H_2C_c)CH_2 - C - C'(e))$	ڻ	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	\$0.04	129.96	22.66	1.94462	0.49298	
$vr(C_{r}C_{r}(H_{2}C_{r}-R)HCH_{2}-C_{r}C_{r}(B)$	ぴ	-0.72457	-0.92918	-0.92918	9	-154,19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279	
$aC_{a}(R-H_{2}C_{a})C_{b}(R^{*}-H_{2}C_{c})CH_{2}-C_{c}$	ڻ	-0.72457	-0.72457	-0,72457	-0.72457	-154.51399	17716.0	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298	
								-							-	

(a) a la coma B) branche (a) como como como como como como como com	10 / 21 / 21								֡		
Parameters	C-S Group	SO Group	(.) _H	GH,	Group	Group	Group	Group	Group	Group	Group
		2	3	2	-	-	-	-	1	1	1
	0	0	2	-	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
	0.66951		_	-	-	ı	1	1	-	1	-
	-	_	-		_	1	-		Ţ	1	
	1	1.20632	0.91771	17716.0	0.91771	0.91771	0.91771	0.91771	0.91771	17716.0	0,91771
	0	0	0	_	-	0	0	0	1		0
	2	4	-	_	-	2	2	2	2	2	2
	0	-	3	2	-	0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	5,0	5.0	0.5
	0.66951	_	-	-	-	-	_	1	1	-	-
V, (el/)	-46.73032	-82.63003	-107.32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29,10112
V, (eV)	8.13401	19.31325	38.92728	25.78002	12,87680	9,33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	12.47306	20.81183	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V. (eV)	-6.23653	-10.40592	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(.10 110] (eV)	0	-11.52126	-15.56407	-15,56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
ΔΕ _{π,νισ} (so no) (eV)	-0.72457	-1.16125	0	0	0	0	0	0	0	0	٥
E. (10 110) (cV)	0.72457	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
E. (n.sw) (eV)	-31.63521	-63.27088	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31,63535	-31,63535
E. (atom - atom, msp3.AO) (eV)	-0.72457	0	°	0	0	-1,85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
E. (sm) (cV)	-32.35994	-63.27074	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33,08452
@ (1015 rad / s)	30.8880	17.6762	24.9286	24.2751	24.1759	9,43699	9.43699	15,4846	9.43699	9,55643	9.55643
E. (eV)	20.33104	11,63476	16,40846	15.97831	15.91299	6,21159	6.21159	10.19220	6.21159	6.29021	6.29021
E, (eV)	-0.28866	-0.21348	-0.25352	-0.25017	-0.24966	-0,16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{kvh}(eV)$	0.08543	0.12832	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312	0.17978	0.09944	0.12312	0.12312 [2]	0.12312
E. (eV)	-0.24595	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E (eV)	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E, [inay] (eV)	-32.60589	-63.56937	-67.92207	-49.80996	-31,70737	-33.59732	-33.49373	-33.24376	-33.59732	-33,18712	-33.18712
Emma (es so no) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Emand (c, so no) (eV)	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
(A) (A)	3 33611	3.86856	12.49186	7.83016	109625	N27751	1 7007 1	2 07208	4 17051	3,62128	2 01734

C-C (f) Table 15.169. The total bond energies of alkyl sulfoxides calculated using the functional group composition and the energies of Table 15.168 compared to the experimental values [3].

Formula Name C = S SO CH, CH, CH, CH C = C (a) C = C (b) C = C (c) C = C (c) C = C (d) C = C (e)

	Exp. θ		96.6 (dimethyl sulfoxia	106.7 (dimethyl sulfoxi	107 (propane)	112 (propane) 113.8 (butane) 110.8 (isobutane)	111.0 (butanc) 111.4 (isobutanc)	110.3 (dimethyl sulfoxío			110.8 (isobutane)		111.4 (isobutane)	111.4 (isobutane)	
	(al. <i>(</i>		96.20	106.88	108.44	110.49	110,49	109.50	109.44	109.44	110.67	110.76	111.27	111.27	107 50
	θ ₁ ©														Ĺ
	e, ()														Ĺ
	θ <u></u> ①	i				69.51	69.51		70.56	70.56					77 50
sp'.40).	E _T (eV)		-1.85836	-1.65376	0	÷		0			-1.85836	0	0	-1.85836	
т – ағот, п	'ئۍ		0.82562	0.87489	1.15796		-	1.15796			0,81549	1.04887	1,04887	1.04887	
t is E _T (alc	ů"			-	0.75			0.75			1	0.75	0.75	0.75	
ere used. 1	ပ်		1	~	J			1			- (	1	~	_	
ing angle w	ڻ			-				_			1	0.75	0.75	0.75	
rom the preced	C ₂ Alom 2		0.82562	0.85395 (Eq. (15.114))				1			0.81549	17716-0	0.91771	17716.0	
e parameters f	C. Alom I		0.82562	0.89582	0.86359			0.86359			0.81549	0.87495	0.87495	0.87495	
lculation of $\theta_{\rm r}$ , th	Atom 2 Hybridization Designation	(Table 15.3.A)	21	0	×			н			25	-	-		
I]. In the ca	E'radositic Alam I		-16.47951	-13,61806 O	H			н			-16.68412 C.	-14.82575 C,	-14.82575	-14.82575 C.	
erimental values	Atom I Hybridization Designation	(Table 15,3.A)	21	2	7			7			25	۶.	5	:c	
ides and exp	Eronianise Atom I		-16.47951	-15.18804 C,	-15.75493			-15.75493			-16 68412 C	-15,55033	-15,53033	-15.55033	
alkyi sulfox	2c' Terminal Aluns (G _o )		4,9800	4.9598	3,4252			3.4252			4.7958	4.1633	4,1633	4.7958	
rameters of	2c' Bend 2 (a ₀ )		3,34541	2,81792	2,11106			2.09711			2.91547	2.11323	2.09711	2.90327	
and angle pa	2c' Bond 1 (a ₀ )		3,34541	3,34541	2.11106			2.09711			2.9(547	2.91547	2.91547	2.90327	
Table 15.170. The bond angle parameters of alkyl sulfoxides and experimental values [1]. In the calculation of P, the parameters from the preceding angle were used. £7 is £7{doin-aron, ansy40},	Atoms of Angle		".X(".)7	05".37	Methytone ZHC "H	*,75°,77	H",",")7	Methyl ZHC "H	7,1,1,7	H", J", J7	ابه در ابه در	".) ^(c) ".) ^(c)	LC, C, H iso C,	اهد ر." حرد "ر." ر.	., ., ., ,

## DIMETHYL SULFOXIDE DIHEDRAL ANGLE

The dihedral angle  $\theta_{ZS=O/CSC}$  between the plane defined by the CSC MO comprising a linear combination of two S-C-bond MOs and a line defined by the S=O-bond MO where S is the central atom is calculated using the results given in Table 15.170 and Eqs. (15.105-15.108). The distance  $d_1$  along the bisector of  $\theta_{ZCSC}$  from S to the internuclear-distance line between C and C,  $2c'_{C-C}$ , is given by

$$d_1 = 2c'_{S-C} \cos \frac{\theta_{\angle CSC}}{2} = 4.9800 a_0 \cos \frac{96.20^{\circ}}{2} = 2.23423 a_0$$
 (15.134)

where  $2c'_{S-C}$  is the internuclear distance between S and C. The atoms C, C, and O define 10 the base of a pyramid. Then, the pyramidal angle  $\theta_{ZCOC}$  can be solved from the internuclear distances between C and C,  $2c'_{C-C}$ , and between C and O,  $2c'_{C-O}$ , using the law of cosines (Eq. (15.106)):

$$\theta_{\angle COC} = \cos^{-1} \left( \frac{\left( 2c'_{C-O} \right)^2 + \left( 2c'_{C-O} \right)^2 - \left( 2c'_{C-C} \right)^2}{2\left( 2c'_{C-O} \right) \left( 2c'_{C-O} \right)} \right)$$

$$= \cos^{-1} \left( \frac{\left( 4.95984 \right)^2 + \left( 4.95984 \right)^2 - \left( 4.9800 \right)^2}{2\left( 4.95984 \right) \left( 4.95984 \right)} \right)$$

$$= 60.27^{\circ}$$
(15.135)

Then, the distance  $d_2$  along the bisector of  $\theta_{\angle COC}$  from O to the internuclear-distance line 15  $2c'_{C-C}$ , is given by

$$d_2 = 2c'_{C-Q}\cos\frac{\theta_{ZCOC}}{2} = 4.95984a_0\cos\frac{60.27^{\circ}}{2} = 4.28952a_0$$
 (15.136)

The lengths  $d_1$ ,  $d_2$ , and  $2c'_{S=0}$  define a triangle wherein the angle between  $d_1$  and the internuclear distance between O and S,  $2c'_{S=0}$ , is the dihedral angle  $\theta_{\angle S=O/CSC}$  that can be solved using the law of cosines (Eq. (15.108)):

$$\theta_{ZS=O/CSC} = \cos^{-1}\left(\frac{d_1^2 + (2c'_{S=O})^2 - d_2^2}{2d_1(2c'_{S=O})}\right)$$

$$= \cos^{-1}\left(\frac{(2.23423)^2 + (2.81792)^2 - (4.28952)^2}{2(2.23423)(2.81792)}\right)$$

$$= 115.74^{\circ}$$
(15.137)

20

The experimental [1] dihedral angle  $\theta_{\rm \angle S=O/CSC}$  is

$$\theta_{\angle S=O/CSC} = 115.5^{\circ} \tag{15.138}$$

SULFITES 
$$(C_n H_{2n+2}(SO_3)_m, n=2,3,4,5...\infty)$$

The alkyl sulfites,  $C_n H_{2n+2}(SO_3)_m$ , comprise a C-O-SO-O-C moiety that comprises two types C-O functional groups, one for methyl and one for alkyl, and O-S and SO functional groups. The alkyl portion of the alkyl sulfite may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in sulfites are equivalent to those in branched-chain alkanes.

The SO functional group is equivalent to that of sulfoxides with  $E_T \left(atom-atom,msp^3.AO\right)=0$  as given in the Sulfoxides section. The methyl and alkyl C-O

15 functional groups having  $E_T(atom-atom,msp^3.AO) = -1.44915 \, eV$  and  $E_T(atom-atom,msp^3.AO) = -1.65376 \, eV$ , respectively, are equivalent to the corresponding ether groups given in the Ethers section except for the energy terms corresponding to oscillation of the bond in the transition state.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  3P_2 . The SO functional group comprises a double bond between the S atom and the two unpaired electrons of O. The S atom also forms single bonds with two additional oxygen atoms that are each further bound to methyl or alkyl groups. The first bond-order bonding in the O-S groups is between the sulfur atom and a O2p AO of each oxygen of the two bonds. The formation of these four bonds with the sulfur atom is permitted by the hybridization of the four electrons of the S3p shell to give the orbital arrangement given by Eq. (15.129). Then, the Coulombic energy  $E_{Coulomb}(S,3sp^3)$  of the outer electron of the  $S3sp^3$  shell given by Eq. (15.120) with  $r_{3sp^3} = 1.17585a_0$  (Eq. (15.119)) is  $-11.57099 \ eV$ . Using Eq. (15.16) with the radius of the

sulfur atom  $r_{16} = 1.32010 a_0$  given by Eq. (10.341), the energy  $E(S3sp^3)$  of the outer electron of the  $S3sp^3$  shell given by the sum of  $E_{Coulomb}(S3sp^3)$  and E(magnetic) is  $E(S3sp^3) = -11.52126 \ eV$  (Eq. (15.130)).

Thus, the O-S group is solved as an energy minimum by hybridizing the four S3p 5 electrons to form a  $S3sp^3$  shell, and the sharing of electrons between the O2p AO and the  $S3sp^3$  HO to form a MO permits each participating orbital to decrease in radius and energy. As in the case of thiols, sulfides, disulfides, and sulfoxides, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus,  $c_1$  and  $c_2$  are equal to one in Eq. (15.52), and the energy matching condition is determined by the  $C_2$  10 parameter. Each  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the S HO has an energy of  $E(S3sp^3) = -11.52126 \, eV$ . To meet the equipotential condition of the union of the O-S  $H_2$ -type-ellipsoidal-MO with these orbitals with the oxygen that further bonds to a  $C2sp^3$  HO, the hybridization factor  $C_2$  of Eq. (15.52) for the O-S-bond MO given by Eqs. 15 (15.68) and (15.70) is

$$C_{2}(S3sp^{3} \text{ to } O \text{ to } C2sp^{3}HO) = \frac{E(S,3sp^{3})}{E(O,2p)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-11.52126 \text{ eV}}{-13.61806 \text{ eV}}(0.91771)$$

$$= 0.77641$$
(15.139)

As in the case of thiols, sulfides, disulfides, and sulfoxides, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the O-S-bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in 20 Eq. (15.42) with E(AO/HO) = 0 and  $E_T(AO/HO) = \Delta E_{H_2MO}(AO/HO)$ . For sulfites,  $\Delta E_{H_2MO}(AO/HO) = -0.92918 \, eV$  and equivalently,  $E_T(atom-atom,msp^3.AO) = -0.92918 \, eV$  (Eq. (14.513)) due to the maximum energy match with the oxygen AO as in the case with carboxylic acid esters.

The symbols of the functional groups of branched-chain alkyl sulfites are given in Table 15.177. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfites are given in Tables 15.178, 15.179, and 15.180, respectively. The total energy of each alkyl sulfite given in Table 15.175 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.180 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfites determined using Eqs. (15.79-15.108) are given in Table 15.182.

Table 15.177. The symbols of functional groups of alkyl sulfites.

Table 13.177. The symbols of functional	groups of any suffices.
Functional Group	Group Symbol
C-O (methyl)	C-O (i)
C-O (alkyl)	C-O (ii)
O-SO ₂	O-S
SO	SO
CH₃ group	$C-H\left(CH_{_{3}}\right)$
CH₂ group	$C-H$ $\left( CH_{2}\right)$
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Table 13.178. The geometrical bond parameters of alkyl sulfites and experimental values [1]													
	C-0 (i) Group	C-O (ii) Group	S-0	so	$C-H\left(CH_3\right)$ Group	$C-H\left(CH_{z}\right)$ Group	dnoıD Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
	1,80717	1.79473	1.70299	1.98517	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2,10725
	1.34431	1.33968	1.48102	1.40896	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
	1.42276	1.41785	1.56744	1.49118	1.10974	1.11713	1.11827	1.54280	. 1.54280	1.53635	1.54280	1.53635	1.53635
	<i>)-</i>		1.574 (H ₂ SO ₄ )	1,485 (dimethyl sulfoxide)	1.107 (C-H propane) (1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (hutane)	1.532 (propane) 1.531	1.532 (propane) 1.531	1.532 (propane) 1.531	1.532 (propane) 1.531
	1.20776	1.19429	0.84069	1.39847	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1 54616	1 52750	(butane)
	0.74388	0.74645	0.86966	0.70974	0.63580	0.63159	0 63095	0.68600	0 68600	000000	000000	000000	0.726.1

Table 15.179. The MO to HO intercept geometrical bond parameters of alkyl sulfi	eometrical t	ond parameters of	es.	K, K, K are $H$ or arkyl groups.		Er IS Er (aroni	dem'mon_	100				-		-	
Bond	Atom	E	E		E	Final Total	, and	fund	Ecaniom	$E(C2sp^3)$	ъ.	Ф, ;	œ" ;	ď	·á' 〔
		(eV) Bond 1	(eV) . Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C2sp³	(a ₀ )	(a ₀ )	(eV) Final	(eV) Final	•	 (e)	 ©	(a _e )	(a _p )
					0	(eV)				†	1	10.00	37.75	1 2000	017130
$(RO)_{L}S=O_{u}$	S	0	-0.46459 :	-0,46459	0		1,32010	0.86359	-15.73493		/8.30	101.44	37.75	1,30020	0.171.0
$(RO), S = O_c$	0	0	0	0	0		000001	17719.0	-14.82575		84,06	95,94	40.75	1.50400	0.09504
CH,OS(O)OR	S	-0.46459	-0,46459	0	0		1,32010	0.86359	-15,75493		126.68	53,32	55.47	0.96521	0,51581
$CH_3O_4 - S(O)OR^4$	o [*]	-0,46459	-0.72457	0	ŋ		000001	0.84957	-16,01492		126.03	53.97	54.81	0.98133	0.49969
RCH ₁ O ₂ – S(O)OR ⁷	0"	-0.46459	-0.82688	0	0		1.00000	0.84418	-16,11722		125.77	54,23	54.56	0.98753	0.49349
H ₃ C _u = 0,S(0)OR	0°	-0.72457	-0.46459	. 0			1.00000	0.84957	-16,01492		93.85	86.13	44.57	1,28731	0.05700
H,C, -0.S(0)0R	. U	-0.72457	0	. 0	0	-152.34026	1,77,10,0	0.87495	-15,55033	-15.35946	95.98	84.02	46.10	1,25319	0.09112
RH ₂ C _x - O _a S(O)OR'	o	-0.82688	-0.46459	0	0		1.00000	0.84418	-16,11722		94.50	85.50	44.80	1.27343	0.06624
RH ₂ C, -0,S(O)OR'	ئ	-0.82688	-0.92918	D	-0	-153,37175	0.91778	0.82053	-16,58181	-16.39095	92.41	87.59	633	130512	0.03456
C-H (CH.)	C	-0.92918	0	0	0	-152.54487	17716.0	0.86359	-15.75493	-15.56407	77.49	102,51	41.48	1,23564	0.18708
C-H (CH.)	ر	-0.92918	-0.92918	0	0	-155.47406	17716.0	0.81549	-16,68412	-16.49325	68.47	111.53	35.84	1.354%6	0.29933
C-H (CH)	ن	0,92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17,61330	-17.42244	61.10	118,90	31.37	1.42988	0,37326
H,C,C,H,CH, -		-0.929(8	0	c	0	-152.54487	17716.0	0.86359	-15,75493	-15.56407	63.82	116.18	30.08	1,83879	0.38106
H,C,C,H,CH,	ر ئ	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16,68412	-16,49325	56.41	123,59	26.06	06806'1	0.45117
$R-H_2C_{G_1}(H_2C_2-R)HCH_2-$	i.t	-0,92918	-0.92918	-0.92918	c	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1,97162	0.51388
$R - H_2C_a(R - H_2C_a)C_b(R^a - H_2C_c)CH_2$	1,	-0.92918	-0.72457	-0,72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_{*}C_{*}(H_{2}C_{*}-R)HCH_{2}-C_{*}C_{*}C_{*}C_{*}C_{*}$	ئن	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
teric, (R'-H ₂ C';)C',(R'-H ₂ C';)CH ₂ - (C-C' (e))	ئ	-0.72457	-0.72457	0.72457	-0.72457	-154.51399	17716.0	0,76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$ter(C_n,C_n(H_2C_n-R)HCH_2-(C-C_n(f))$	ئ	-0.72457	-0.92918	-0.92918	9.	-154.19863	0.91771	0,78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$ksoC_{\mu}(R^{*}-H_{2}C_{\mu})C_{\mu}(R^{*}-H_{2}C_{\mu})CH_{2}-C_{\mu}CH_{2}C_{\mu}$	ئ ^ئ 	-0,72457	-0.72457	-0.72457	-0.72457	-154,51399	0.91771	0.76765	-17,92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
	-														

He 15.179. The MO to HO intercept geometrical bond parameters of alkyl sulfites.  $R_tR^t$ , are H or alkyl groups.  $E_t$  is  $E_T(atom-atom,msp^t,AO)$ .

							-	300	300	(3) (1)	5010		ì
Parameters	(E) 0-0	C-0(II)	5-0	SO	CH,	(H)	E C	C-C (a)	(a) (b) (c) (d)	(a)	Carolin (4)	Grown	Group
	Group	Group	Group	Group	Group	Group	dinoin	dion	diolo	dans	A STATE OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PAR		
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·	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.0	CO	C'A		CO
ť	_	-	0.77641	-	-	1	1	1	-	-	-	1	-
	-	_	-			_	-	П	1	_		1	I
	0.85395	0.85395		1.20632	17710	0,91771	17710	0.91771	17716	17716.0	12210	17716.0	17716.0
	0	0	0	0	0	-		0	0	0	1	1	0
<i>i</i> :	,	2	2	4	1		-	2	2	2	2	2	2
7	c	c	0	,	3	2	-	0	0	0 .	0	0	0
	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	5.0	0.5
*	-	-	0.77641	-	1	1	-	-	1	1	1	1	-
V (aV)	-33,15757	-33.47304	-48.93512	-82.63003	-107,32728	-70.41425	-35,12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V (eV)	10,12103	10.15605	9.18680	19.31325	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	9.17389	9.32537	14.36741	20.81183	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_ (eV)	-4.58695	-4.66268	-7.18371	-10.40592	-16,26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(.v 10) (eV)	-14.63489	-14.63489	0	-11.52126	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
ΔΕ _{H,MO} (40 m) (eV)	-1.44915	-1.65376	-0,92918	-1,16125	0	0	0	0	0	0	0	0	٥
E. (no no) (eV)	-13,18574	-12.98113	0.92918	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
E. (n.10) (eV)	-31,63533	-31.63544	-31.63543	-63.27088	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
E. (alont - alom, msp. AO) (eV)	-1,44915	-1.65376	-0.92918	0	0	0	0	-1.85836	-1.85836	-1.44915	-1,85836	-1.44915	-1.44915
$E_r(in)$ $(eV)$	-33,08452	-33.28912	-32.56455	-63.27074	-67,69450	-49.66493	-31.63537	-33.49373	-33,49373	-33.08452	-33,49373	-33.08452	-33.08452
ω (1015 rad / s)	22,0240	12.1583	33.4164	17.6762	24.9286	24.2751	24.1759	9.43699	9,43699	15.4846	9.43699	9.55643	9.55643
E. (eV)	14,49660	8,00277	21.99527	11,63476	16.40846	15.97831	15.91299	6,21159	6.21159	10.19220	6.21159	6.29021	6.29021
F (eV)	-0.24921	-0.18631	-0.30214	-0.21348	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Krib}$ (eV)	0.13663	0.13663	0.08679	0.12832	0.35532	0.35532 (Fo (13.458))	0.35532 (Fa (13.458))	0.12312	0.17978	0.09944	0.12312	0,12312	0.12312
E (eV)	-0.18089	-0.11799	-0.25875	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E (eV)	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803
E. Group (eV)	-33,26541	-33.40711	-32,82330	-63.56937	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33,18712	-33.18712
E . (e, 40 no) (eV)	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489
E (c. 10 110) (eV)	0	0	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
(10)	3,99563	4.13733	3.55352	3.86856	12.49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	3,91734

Table 15.181. The total bond energies of alke/f sulfites calculated using the functional group composition and the energies of Table 15.180 compared to the experimental values [3].

Formula Name C = C (i) C = C (ii) C = C (ii) C = C (ii) C = C (iii) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C = C (iv) C =

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	Exp. θ (°)				,	107 (propanc)	(propane) 113.8 113.8 (butane) 110.8	(butanc) (butanc) (11.4	(isobutane)			[10.8 (isobutane)		(11.4 (isobutane)	(isobutane)	
	Cal. <i>θ</i>		108.46	103.35	117,84	108.44	110.49	110.49	109.50	100,44	1004	110.67	97.011	111.27	111.27	107.50
	ξ _θ (ο)															
	θ ©				_											
	θ (0)				-	-	15.09	69.51	1	70.56	70.56					72.50
?.40).	(eV)		-1.65376	-1.65376	-0.72457	0			0			-1.85836	0	0	-1.85836	
ı – atonı, nısp	''ئ		0.84835	0.84418	0.82000	1.15796			1.15796			0,81549	1.04887	1,04887	1.04887	
is $E_T(atom)$	. 5		-	-	_	0.75			0.75			_	0.75	0,75	0.75	
e used. Er	ڻ		_	_	0,77641 (Eq.	1			-			-	_	_	-	
ig angle wer	J.		_		_	1						-	0.75	0.75	0.75	
n the precedir	C ₂ Λίοπι 2		0.84418	0.84418	0.77641 (Eq. (15.139))	-			_			0.81549	0,91771	17710.0	17716.0	
arameters fro	C ₂		0.85252	0.84418	0.86359	0.86359	r		0.86359			0.81549	0.87495	0.87495	0.87495	
lation of $\theta_r$ , the p	Atom 2 Hy bridization Designation	(Table 15.3.A)	=	Ξ	S	Ξ			=			25	_	_	_	
In the calcu	E Cratonine Atom 2	6671131.	o"	-16.11722	-10,36001	#	- 0		Ŧ		í	-16.68412	-14.82575 (',	-14.82575 (°,	-14.82575 C,	
mental values [1]	Atom I Hybridization Designation	(Table 15.3.A)	G	. н		7		:	7			22	ŝ	•0	'n	
s and expen	Econtombic Alon 1	-15 95954	0	-16.117 <u>22</u> O ₄	-15.75493	-15.75493			-15,75493			-16.68412 C,	-15.55033	-15.55033	-15.55033 (° _b	
alkyl sulfite	2c' Teminal Atoms (q ₀ )		4.6904	4.6476	917874	3.4252			3.4252			4.7958	4.1633	4.1633	4.7958	
rameters of	2c' Brad 2 (a,)		2.96203	2.96203	2,96203	2.11106			2.09711			2.91547	2.11323	2.09711	2.90327	
ond angle pa	2c' Bond 1 (a ₀ )		2.81792	2,96203	2.68862	2,11106			2.09711			2.91547	2.91547	2.91547	2.90327	
Labor 15.102. The bond angle parameters of alkyl suffice and experimental values [1]. In the calculation of $ heta_c$ , the parameters from the preceeding angle were used. $E_f$ is $E_f$ (oran – atom, msp. $AO$ )	Alimin of Angle		70°,07	ZO,,XO,	S,0,72	Mehylene ZHC, H	דנ"נ.'נ	H', ,", )7	Methy I ZHC "H	לכ"כ"כ"	H,","	''.''.''.'' '''.''.''.''	Z(', C', H in C',	".) ⁽⁵⁾	لار الر"ر" ادما لا"	7,5°,5°,7

SULFATES 
$$(C_n H_{2n+2} (SO_4)_m, n = 2,3,4,5...\infty)$$

The alkyl sulfates,  $C_n H_{2n+2} (SO_4)_m$ , comprise a  $C-O-SO_2-O-C$  moiety that comprises two types C-O functional groups, one for methyl and one for alkyl, and O-S and  $SO_2$  functional groups. The alkyl portion of the alkyl sulfate may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in sulfates are equivalent to those in branched-chain alkanes.

The methyl and alkyl C-O functional groups having  $E_T(atom-atom,msp^3.AO)=-1.44915\ eV$  and  $E_T(atom-atom,msp^3.AO)=-1.65376\ eV$ , 15 respectively, are equivalent to the corresponding groups given in the Sulfites section. The O-S functional group having  $E_T(atom-atom,msp^3.AO)=-0.92918\ eV$  is equivalent to that given in the Sulfites section. The  $SO_2$  functional group is equivalent to that of sulfones with  $E_T(atom-atom,msp^3.AO)=0$  as given in the Sulfones section.

The symbols of the functional groups of branched-chain alkyl sulfates are given in Table 15.183. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfates are given in Tables 15.184, 15.185, and 15.186, respectively. The total energy of each alkyl sulfate given in Table 15.187 was calculated as the sum over the integer multiple of each  $E_D$  (circup) of Table 15.186 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfates determined using Eqs. (15.79-15.108) are given in Table 15.188.

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Table   15.183. The symbols of functional groups of alkyl surfates.   Emetional Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Group   Grou	55	Group Symbol	CO (i)	(1)	S=0	So ₂	$G - H$ $(CH_3)$	$C - H(CH_s)$	7 = 1.	(6)	(E) (F)	(a) (b) (c) (c) (d)	(a)	(a) (b)	(i) (i=1)
	Table 15.183. The symbols of functional groups of alkyl sulf.	Functional Group				SO,						CC bond (tert-C)	CC (iso to iso-C)	CC (t to t-C)	CC (t to iso-C)

Ę	Doromotor	Parameter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commenter   Commen	מסוות משוובינבים חו		-									
	aratifeter.	Group	Group	\$-0	Š	C-H (CH ₃ )	$C-H(CH_2)$	C-H Group	C-C (a) Group	C-C (b) Groun	(a) 2-2	C-C (d)	(e) 2~2	(t) 2-2
,	a (a)	1.80717	1.79473	1 70799	1 85951	0000	dioni		.			dron	dinto	Croup
L					1.00.01	1.04720	1.0/122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
	( (a ₀ )	1.344.51	1.33968	1.48102	1,36327	1.04856	1.05553	1.05661	1.45744	1 45744	1 45164	1 45744		
_	Bond				1.						1.42104	1,43/44	1.45164	1.45164
- 7	Length 2c' (A)	1.42276	1.41785	1.56744	1.44282	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
	Exp.	ψ.												
	Bond Length			1.574 (H.SO.)	1.435 (dimethyl	(C-H propane)	e) (C-H propane)	1.122	1.532 (propane)	1.532 (propane)	1.532 (propane)	1,532 (propane)	1.532 (propane)	1.532
	<u>F</u>	-		,	sulfone)	(C-H butane)	(C - H butane)		1.531 (butane)	1.531 (hutane)	1.531 (furtrue)	1.531	1.531	1.531
4	1,c (a)	1.20776	1.19429	0.84069	1.26315	1.27295	1.29569	1 20074	1 \$4616	1 64616	Courage	(outains)	(butane)	(butane)
_	œ.	0.74388	0.74645	0,86966	0.73353	0.63580	0 62150	20000	210101	UTO#C")	1.52750	1.54616	1.52750	1.52750
						200000	4.02.22	0.0500	0.08000	0.68600	0 68888	007070	000070	00000

Table 15.185. The MO to HO intercept geometrical bond parameters of alkyl suitates. 14,	netrical bon	d parameters of .	alkyi shirares.	K,K are n	or ankyr groups.	Ly 13 Ly (mon	$c_T \approx c_T (arom - arom, msp. ac)$									
Bond	Atom	$E_T$	Er	E	E	Final Total	Franci	Fruil	Ecodomia	$E(C2sp^3)$	ι,θ	θ	θ,	ď,	d,	
		(eV) Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C2sp ³	(a ₀ )	(a _a )	(eV) Final	(eV) Final	©	<u> </u>	©	(°)	(a ₀ )	
$(RO), (O_n)S = O_n$	S	0	0	-0.46459	-0.46459		1.32010	0.86359	-15.75493		90.46	89.54	43.13	1,35635	0.00693	
$(RO), (O_a)S = O_a$	0,	0	0	0	0		1.00000.	17716,0	-14,82575		95.05	84.95	46.36	1.28256	0.08071	
CH,O, -5(O2)OR'	s	-0.46459	-0.46459	0	0		1.32010	0.86359	-15.75493		126.68	53.32	55.47	0.96521	0.51581	
$CH_1O_a - S(O_1)OR'$ (C - O (i))	0,	-0,46459	-0.72457	0	0		1.00000	0,84957	-16.01492		126.03	53.97	54.81	0.98133	0.49969	
$RCH_2O_a - S(O_2)OR^{-1}$ (C - O (ii))	0,	-0.46459	-0.82688	0	0		1.00000	0.84418	-16.11722		125.77	54.23	54.56	0.98753	0.49349	
$H_3C_s - O_sS(O_2)OR$	0,	-0.72457	-0,46459	. 0.	. 0		1.00000	0.84957	-16.01492		93.85	86.15	44.57	1.28731	0.05700	
$H_3C_s - O_sS(O_2)OR$ (C - O (i))	ు	-0.72457	0	0	0	-152.34026	17719.0	0.87495	-15,55033	-15.35946	95.98	84.02	46,10	1.25319	0.09112	
$RH_2C_s - O_sS(O_2)OR'$ (C - O (ii))	o"	-0 82688	-0.46459	. 0	0	5 -	1.00000	0.84418	-16.11722		94.50	85.50	44.80	1.27343	0.06624	-
$RH_2C_s - O_sS(O_2)OR$	UT	-0.82688	81676'0-	0	0	-153,37175	17710.0	0,82053	-16.58181	-16.39095	92.41	87.59	43.35	1.30512	0.03456	
C-H (CH ₃ )	i	-0,92918	0	0	0	-152,54487	17716,0	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708	
('-H (CH ₂ )	Ü	-0.92918	-0.92918	0	0	-153.47406	17719.0	0,81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933	
('-H (CH)	Ü	-0.92918	-0.92918	-0.92918	0	-154,40324	17716.0	0.77247	-17.61330	-17.42244	61.10	118.90	31,37	1.42988	0.37326	
$\frac{H_3C_6C_8H_2CH_2-}{(C-C_5(a))}$	<i>"</i>	-0.92918	0	0	. 0	-152,54487	17710	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106	
$H_3C_aC_bH_2CH_2 - (C-C_5a)$	ť	-0.92918	-0.92918	0	0	-153,47406	17710.0	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117	
$R - H_2 C_s C_s (H_2 C_s - R^s) H C H_2 - (C - C^s)$	c,	-0.92918	-0.92918	-0.92918	0	-154,40324	17716.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388	
$R - H_2C_s(R^* - H_2C_s)C_s(R^{n-} - H_2C_s)CH_2 - (C - C_1C_2)$	Ċ,	-0.92918	-0.72457	-0.72457	-0.72457	-154,71860	17710	0.75889	-17,92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570	
$isoC_{\alpha}C_{\mu}(H_{\alpha}C_{\alpha}-R^{\alpha})HCH_{\alpha}-(C-C^{\alpha}(d))$	ڻ'	-0.92918	-0.92918	-0.92918	0	-154.40324	17710	0.77247	-17,61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388	
$ler(C_a(R^1 - H_2C_4)C_5(R^{n-1} + H_2C_5)CH_2 - (C^1 - C^2))$	, C,	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	17710.0	0.76765	-17.92866	-17.73779	50.04	129.96	27.66	1.94462	0,49298	
$turtC_sC_k(H_2C_s - R)HCH_2 - (C - C'(f))$	<b>್</b>	-0.72457	-0.92918	-0.92918	-0,	-154.19863	17716.0	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279	
$ixoC_{\mu}(R^{n} - H_{2}C_{\mu})C_{\mu}(R^{n} - H_{2}C_{\mu})CH_{2} - (C - C^{n}(f))$	.5	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17710	0.76765	-17.92866	-17,73779	50.04	129.96	22.66	1.94462	0.49298	

Parameters				~						3	3:10	(0)	(F)
	(i) 0-0	C~0 (ii)	0-S	, S	(H)	(.H ₂	ביי ביי	Groun	Groun	S Louis	Group Group	Group	Grown
	Group	Croup	Croup	Group	Group	Group	dioni	dion	dingin	dipolio	dinair	distri	dana
n,	-	_		4	3	7	-	-		-	1	1	1
n,	0	0	0	0	2	1	0	. 0	0	0	0	0	0
n,	0	0	0	0	0	0	0	0	0	0	0	0	0
(;	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	5.0	5.0	0.5	6.5	0.5
(;	_	-	0.77641		-	-	-	-	-		-	_	_
, v	_	-	_	-	-	-	1			-	1	_	-
ร	0.85395	0.85395	-	1.20632	0.91771	17716.0	17716.0	- 117160	17716.0	0.91771	0.91771	0.91771	0.91771
. 5	0	0	0		0	_	1	0	0	0	1	1	0
5	2	2	2	8	_		1	2	2	2	2	2	2
	0	0	0		3	2	-	0	0	0	0	0	0
	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	5.0	0.5
ئ.	_	-	0.77641		_	-	ı	-	-	1	1	1	1
V, (eV)	-33.15757	-33.47304	-48.93512	-180.36454	-107.32728	-70.41425	-35,12015	-28.79214	-28.79214	-29.10112	-28.79214	-29,10112	-29.10112
V, (aV)	10,12103	10.15605	9.18680	39,92103	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9,33352	9.37273	9.37273
T (eV)	9.17389	9,32537	14,36741	48.52397	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V, (eV)	4.58695	-4.66268	-7.18371	-24.26198	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3,45250
E(.10 110) (eV)	-14.63489	-14,63489	0	-11.52126	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
ΔΕ _{π. 310} (.10 110) (eV)	-1.44915	-1.65376	81626:0-	-1.16125	0	0	. 0	0	0	0	0	0	0
Er (so no) (eV)	-13.18574	-12,98113	0.92918	-10,36001	-15.56407	-15,56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15,35946
$E_r(n_i, n_i)$ (eV)	-31,63533	-31,63544	-31.63543	-126.54154	-67.69451.	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31,63535
$E_T(atom - atom, mxp^3, AO)$ (eV)	-1.44915	-1,65376	-0.92918	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1,44915
E, (110) (eV)	-33.08452	-33,28912	-32.56455	-126.54147	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
a (1015 rad / s)	22,0240	12.1583	33.4164	11.5378	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
Er (eV)	14.49660	8.00277	21.99527	7.59437	16,40846	15.97831	15.91299	6.21159	621159	10.19220	6,21159	6.29021	6,29021
$\vec{E}_n$ (cV)	-0.24921	-0.18631	-0.30214	-0.17247	-0.25352	-0.25017	-0.24966	51591'0-	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Kirb}$ (eV)	0.13663	0.13663	0.08679	0.12832	0.35532 (Eq. (13,458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978	0.09944	0.12312	0.12312	0.12312
E (eV)	-0.18089	-0.11799	-0.25875	-0.10831	-0.22757	-0.14502	-0.07200	-0,10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E. (eV)	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_r(viral)$ (eV)	-33.26541	-33.40711	-32.82330	-126.97472	-67.92207	-49.80996-	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E total (c. 40'10) (eV)	-14.63489	-14,63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Emmissi (c. 30'10) (eV)	0	0	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
F (c ) (aV)	3 99563	4.13733	3,55352	8.61994	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

able 13.1 to Compared 10 life experimental values 13. C-C (d) C-C (e) C-C (f) C-C (f) C-C (f) group composition and the energies of  $SO_2$   $CH_3$   $CH_2$   $CH_2$ 

Table 15.187. The total bond energies of allyl sulfates calculated using the function C-O (i) C-O (ii) O-S Group Group Group

		1									-	713				
Exp. θ · · (°)		120.9 [44] (dímethyl sulfate)	109.67 [44] (dimethyl sulfate)	103.85 [44] (dimethyl sulfate)	117.43[44] (dimethyl sulfate)	107 (propane)	112 (propane) 113.8 (butane) 110.8 (fsobutane)	111.0 (butane) 111.4 (isobutane)				110.8 (isobutane)		111,4 (isobutane)	111.4 (isobutane)	
(°)		120.44	110.26	103.35	117.84	108.44	110.49	110.49	109.50	109,44	109.44	110.67	110.76	111.27	111.27	107.50
(e) g																
6 0	1		,													
φ (0)	+						69.51	69.51		70.56	70.56					72.50
E _T (eV)		-1.65376	-1.65376	-1,65376	-0.72457	0			0			-1.85836	0	0	-1,85836	
٠٠٠		0.85252	0.84835	0.84418	0.82000	1.15796	, -		1.15796			0.81549	1.04887	1.04887	1.04887	
<b>ল</b>		-		- *	1	0.75			0.75			_	0.75	0.75	0.75	
౮		<b>-</b> ¢	_	1	0.77641 (Eq. (15.139))	_			-			-	-	_	-	
לי		-,	-	1					-			-	0.75	0,75	0,75	
C ₂		0.85252	0.84418	0.84418	0.77641 (Eq. (15.139))	_			.1	·	,	0.81549	1771	0.91771	0.91771	
C ₂		0.85252	0.85252	0.84418	0.86359	0.86359			0,86359			0.81549	0.87495	0.87495	0.87495	
Atom 2 Hybridization Designation	(Table 15.3.A)	. 6	=	11	s	н		·	н			25	_	_	J	
F. intombe Atom 2	1,00000	-13.93934 O _h	-16.11722 O	-16.11722 O _d	-10.36001 .S	ж			я			-16.68412 C.	-14.82575 C _h	-14.82575 C_	-14.82575 C _e	.*
Atom J Hybridization Designation	(Table 15.3.A)	9	6	11	7	7			7			25	5	5	S	
f. Contrastar Atan 1	13000	.15.95954	-15.95954	-16.11722	-15 75493	-15.75493			-15.75493			-16,68412 C,	-(5,55033 C.	-15,55033 C,	-15,55033 C _k	
2c' Tenuinal Atoms ( a _# )		4.7329	4.66%	4.6476	4.8416	3.4252			3.4252			4,7958	4,1633	4,1633	4.7958	
2c' Bond 2 (a _n )		2.72654	2.96203	2.96203	2.96203	2,11106			2,09711			2.91547	2.11323	2.09711	2.90327	
2c' Band 1 (a)		2.72654	2.72654	2.96203	2.68862	2.11106			2,09711			2.91547	2.91547	2.91547	2.90327	
Atuns of Angle		,02,02	°08'07	"os'07	8,0,32	Methylone ZHC,H	; 35'5'37	Н,2,™	Methyl ZHC,H	'J'J'J7	H, 7, 72	20",2";2"	н", Э от Рго С."	LC,C,H	رد رد رد در رد رد	ZC.C.C.

NITROALKANES 
$$(C_n H_{2n+2-m} (NO_2)_m, n = 1, 2, 3, 4, 5...\infty)$$

The nitroalkanes,  $C_n H_{2n+2-m} (NO_2)_m$ , comprise a  $NO_2$  functional group and a C-N functional group. The alkyl portion of the nitroalkane may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and 5 methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in nitroalkanes are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^22s^22p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  3P_2 . The electron configuration of nitrogen is  $1s^22s^22p^3$ , and the orbital arrangement given by Eq. (10.134) has 15 three unpaired electrons corresponding to the ground state  ${}^4S_{3/2}^0$ . The bonding in the nitro  $(NO_2)$  functional group is similar to that in the  $SO_2$  group given previously. It also has similarities to the bonding in the carbonyl functional group. In the  $NO_2$  group, the two unpaired electrons of the O atoms form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a linear combination of two bonds, each of bond order two involving the 20 nitrogen AOs and oxygen AOs of both oxygen atoms. The nitrogen atom is then energy matched to the  $C2sp^3$  HO. In nitroalkanes, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), the N AO has an energy of  $E(N) = -14.53414 \, eV$ , and the O AO has an energy of  $E(O) = -13.61806 \, eV$  [38]. To meet the equipotential condition of the union of the N = O bond MO given by Eqs. (15.68) and (15.70) is

$$c_{2}(O \text{ to } N2p \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(N)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-14.53414 \text{ eV}}(0.91771)$$

$$= 0.85987$$
(15.140)

Since there are two O atoms in a linear combination that comprises the bonding of the  $NO_2$  group, the unpaired electrons of each O cancel each others effect such that  $E_{mag}$  is not subtracted from the total energy of  $NO_2$ . Additionally,  $E_T(atom-atom, msp^3.AO) = -3.71673 \ eV = 4(-0.92918 \ eV)$  (Eq. (14.513)) is the maximum given the bonding involves four electrons comprising two bonds, each having a bond order of one.

The C-N group is equivalent to that of primary amines except that the energies corresponding to vibration in the transition state are matched to a nitroalkane and  $\Delta E_{H_2MO} \left(AO/HO\right) = -0.72457 \ eV$  for nitroalkane and  $\Delta E_{H_2MO} \left(AO/HO\right) = -1.44915 \ eV$  for primary amines. Whereas,  $E_T \left(atom-atom,msp^3.AO\right) = -1.44915 \ eV$  for both functional groups. This condition matches the energy of the C-N group with the  $NO_2$  having  $\Delta E_{H,MO} \left(AO/HO\right) = 0$ .

The symbols of the functional groups of branched-chain nitroalkanes are given in Table 15.189. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 15 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of nitroalkanes are given in Tables 15.190, 15.191, and 15.192, respectively. The total energy of each nitroalkane given in Table 15.193 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.192 corresponding to functional-group composition of the molecule.  $E_{mag}$  given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of nitroalkanes determined using 20 Eqs. (15.79-15.108) are given in Table 15.194.

Table 15.189. The symbols of functional groups of nitroalkanes.

Table 15.165. The symbol	
Functional Group	Group Symbol
NO₂ group	$NO_2$
C-N	C-N
CH ₃ group	$C-H\left(CH_{3}\right)$
CH ₂ group	$C-H(CH_2)$
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

										_
900	_ (€) (1, (€)	Group	2.10725	1,45164	1.53635	1.532	(propane) 1,531	(butane)	1.52750	0.68888
300	(e)	Group	2.10725	1.45164	1.53635	1.532	(propane) 1.531	(butane)	1.52750	0.68888
2,00	(a)	Group	2.12499	1.45744	1.54280	1.532	(propane) 1.531	(butane)	1.54616	0.68600
1,50	(6)	Group	2.10725	1,45164	1.53635	1,532	(propane)	(outane)	1.52750	0.68888
	(a)	Group	2.12499	1.45744	1.54280	1,532	(propane)	(butane)	1,54616	0.68600
	(, =(, (a)	Group	2.12499	1,45744	1.54280	1,532	(propane)	(butane)	1.54616	0.68600
	(;-H	Group	1.67465	1.05661	1.11827		1.122	(ammoori)	1.29924	0.63095
	(H)	Group	1.67122	1.05553	1.11713	1.107	S.	(C - H butane)	1.29569	0,63159
	(-H (CH.)	Group	1.64920	1.04856	1.10974	1.107	an)	(C-H butane)	1.27295	0.63580
The statements of the	C∨	Group	1.97794	1.40639	1.48846			(mechane)	1.39079	0.71104
able 15:120: The Economical bond parameters of min	W	Group	1,33221	1.15421	1,22157		1.224	(mironnemane)	0.66526	0.86639
1 4010 12.170.	Parameter		a (a ₀ )	c' (a ₀ )	Bond Length $2c'$ $(\mathring{A})$	E.m.	Length	(F)	h,c (a,)	e

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	W	O 2	2007/0	51078							,			7	16	;			٠,				PCT	/US2
				· ·			•				·	-						٠					-	
								$\begin{pmatrix} d_2 \\ (a_0) \end{pmatrix}$	0,61333	0,51864	0.14484	0.27620	0.21422	0.18708	0,29933	0.37526	0.38106	0.45117	0.51388	0.50570	0,51388	0,49298	0.47279	0.49298
								(a ₀ )	0,54089	0.63558	1,55123	1.68259	1.62061	1,23564	1.35486	1,42988	1.83879	1.90830	1,97162	1.95734	1,97162	1.94462	1.92443	79446.1
Group Group	2.10725	1,45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888		(o)	50.99	61.50	38.35	31.71	34.98	41.48	35.84	31.37	30.08	26.06	21.90	21.74	21.90	22.66	24.04	22.66
	22	164			750	888		9° ©	44.75	48.43	99.53	110.70	105.04	102.51	111.53	118.90	116.18	123.59	131.70	131.79	131.70	129.96	127.22	129.96
C-C (e) Group	2.10725	1,45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888		, ₀	135,25	131.57	80.47	69,30	74.96	77.49	68.47	61.10	63.82	56.41	48.30	48.21	48,30	50.04	52.78	50.04
C-C (d) Group	2.12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	0.68600		$E(C2xp^3)$ (eV) Final			-15,35946		-16,28864	-15,56407	-16.49325	-17.42244	-15.56407	-16,49325	-17.42244	-17.73779	-17.42244	-17.73779	-17.21783	-17.73779
C~C (c) Group	2.10725	1.45164	1.53635	1,532 (propane) 1,531 (butane)	1.52750	0.68888		Ecusions (eV) Final	-15.75493	-17.40869	-15.55033	-17.40869	-16.47951	-15.75493	-16.68412	-17.61330	-15,75493	-16,68412	-17,61330	-17.92866	-17,61330	-17.92866	-17.40869	-17,92866
					$\vdash$	$\left  \cdot \right $	40}.	" from (a ₀ )	0 86359	0.78155	0 87495	0.78155	0.82562	0.86359	0.81549	0.77247	0,86359	0.81549	0.77247	0 75889	0.77247	0.76765	0.78155	0.76765
C-C (b) Group	2.12499	1.45744	1.54280	1.532 (propane) 1.531 (futane)	1,54616	0.68600	ı — atom, msp³.	(a ₀ )	1.00000	0.93084	17710,0	0,93084	17710.0	17710.0	17716.0	17716.0	17716.0	12216.0	0.91771	0.91771	0,9177!	0.91771	0.91771	0.91771
C'-C'(a) Group	2.12499	1,45744	1,54280	1.532 (propane) 1.531 (futane)	1.54616	0.68600	$E_{\tau}$ is $E_{\tau}(atom-atom,msp^3.AO)$	Final Total Energy C2xp*	(40)		-152,34026		-153.26945	-152,54487	-153.47406	-154,40324	-152.54487	-153.47406	-154,40324	-154.71860 -	-154,40324	-154.51399	-154.19863	-154.51399
	1.67465	- 199		1.122 (isobutane)	1.29924	095	alkyl groups.	(eV) Bond 4	0	-	0	0	-	o	٥	o	0	e	0	-0.72457	0	-0.72457	0	-0.72457
(:-H)	1.67	1.05661	1.11827			0.63095	R, R', R" are H or alkyl	E ₇ (eV) Bond 3	0	-0.72457	0	-0,72457	c	5	0	-0.92918	0	C	-0.92918	-0.72457	-0.92918	-0.72457	-0.92918	-0.72457
$C - H \left( CH_2 \right)$ Group	1.67122	1.05553	1.11713	1.107   (C ~ H propane)   1.117	1.29569	0,63159	troalkanes. R, h	E ₇ (eV) Bond 2	-	-0.92918	0	-0.92918	-0.92918	0	-0.92918	-0.92918		-0.92918	-0.92918	-0.72457 ·	-0,92918	-0.72457	-0.92918	-0.72457
$C - H \left( CH_3 \right)$ Group	1,64920	1.04856	1.10974	1.107 (C-H propane) 1.117	1,27295	0.63580	parameters of ni	E _T (eV) Bond I	0.07018	-0,92918	-0.72457	-0.92918	-0.72457	-0.92918	-0.92918	-0,92918	-0.92918	-0,92918	-0.92918	-0.92918	-0.92918	-41,72457	-0,72457	-0.72457
C-N Group	1.97794	1.40639	1.48846	1.489 (uitromethane)	1.39079	0.71104	reometrical bond	Atom		2 2	ز	×	5			i	ئن	ڻ	ڻ	ئ ا	ť	ڻ	ئ	ئن
Parameter $NO_2$ $C-N$ $C-H$ $(CH_3)$ $C-H$ $(CH_4)$ $C-H$ $(CH_4)$ $C-H$ $(CH_4)$ $CHOUP$	1,33221	1.15421	1.22157	1.224 (nitromethane) (nitr	0.66526	+	Table [5,19]. The MO to HO intercept geometrical bond parameters of nitroalkanes.												- R') HC'H ₂ -	$R = H_2C_a(R - H_2C_d)C_b(R^a - H_2C_c)CH_2$	)HCH ₂ -	, (R"-H2C,)CH2-	) HC'H ₂ –	,(R"-H2C,)CH2-
Parameter	a (a ₀ )	_	Bond Length 1 2c' (A)	-	.	+	Table 15,191. The N	Bond	O= WIND	RN(0) = 0	H,C-NO2	RH,C-NO,	-H,C,-NO,	C-H (CH3)	C-H (CH3)	C - H (CH)	$H_{\lambda}^{C}(C, H_{\lambda}^{C}(H_{\lambda}))$	H,C,C,H,CH, -	$R = H_2 C_s C_b (H_2 C_s - R^2) H C H_2 - C_2 (C_s - C_2)$	$R - H_2C_*(R' - H_2C_*)$	isot. C. (H2C, -R)HCH2-	$(C_{(a)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, C_{(b)}, $	$ler(C_{r}(H_{2}C_{s}-R)HCH_{2})$	$kso(\frac{t}{u}(R^{n} - H_{2}C_{s})C_{R}(R^{n} - H_{2}C_{s})CH_{2}$

	Groun	Group	$CH_{\lambda}$	CH ₂	Group	Group	Group	Group	Group	Group	Group
11.	2	-	3	2	-	-	1	_	1	1	1
,	0	0	2	-	0	0	. 0	0	0	0	0
n,	0	0	0	0	0	0	0	0	0	0	0
ر.	0.5	0.5	0.75	0.75	0.75	0.5	6.5	0,5	0.5	0.5	0.5
	-	-	-	-	_	1	1	I	-	1	
<i>c</i> ,	-	-	_	-	-	-	-	1	1	-	-
3	0.85987	0.91140	17710	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	17716.0	0.91771
£.	0	0	0	1	-	0	0	0	1	1	0
<i>c</i> ,	4	2	_	1	-	2	2	2	2	2	2
C.	0	0		2	_	0	0	0	0	0	٥
	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	6.5	0.5	0.5
	-	-	-		-	-	1		1	-	-
V (eV)	-106.90919	-31,36351	-107.32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29,10112	-29.10112
V, (eV)	23.57588	9.67426	38.92728	25.78002	12,87680	9.33352	9.33352	9.37273	9.33352	9.37273	-9.37273
" (eV)	40.12475	7.92833	32,53914	21.06675	10,48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_ (eV)	-20.06238	-3.96416	-16,26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3,38732	-3.45250	-3,45250
E(so no) (eV)	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-15.35946
$\Delta E_{H,MD}(100\ m)$ (eV)	0	-0.72457	0	0	0	0	0	0	0	0	0
Er (50 110) (eV)	0	-13.91032	-15,56407	-15,56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
Er (u,in) (eV)	-63.27093	-31.63540	-67.69451	-49.66493	-31,63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_r(atom - atom, msp^3.AO)$ (eV)	-3.71673	-1,44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
E. (10) (eV)	-66.98746	-53.08452	-67.69450	-49.66493	-31,63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
@ (1015 rad / s)	19.0113	10.5087	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9,55643	9,55643
E. (eV)	12,51354	6.91703	16.40846	15.97831	15.91299	6,21159	6.21159	10.19220	6.21159	6.29021	6.29021
" (eV)	-0,23440	-0.17214	-0.25352	-0.25017	-0,24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{\chi_{ab}}$ (eV)	0.19342	0.10539	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12512 [2]	0.17978 [4]	0.09944 [5]	0.12512	0.12312 [2]	0.12312
Ene (eV)	-0.13769	0.11945	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{\text{neg}}$ (eV)	0,11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Er (Graup) (eV)	-67.26284	-33.20397	-67.92207	-49.80996	-31,70737	-33.59732	-33.49373	-33.24376	-33.59732	-33,18712	-33,18712
E. (e. 10 10) (eV)	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
E 100 (ct. 10 110) (cV)	0	0	-13.59844	-13,59844	-13,59844	0	0	٥	0	0	0
	000000	01110	20101 01	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,							

Table 15.193. The total bond energies of nitroalkanes calculated using the functional group composition and the energies of Table 15.192 compared to the experimental values [3]. The magnetic energy E_{low} that is subtracted from the weighted sum of the

Formula	Name	MO,	C-N	CH,	CH,	Н.)	('-(' (a)	C-C (b)	(c-(c)	C~C (d)	C-C (e)	C-C (t)	. E.	Calculated Tetal Band	Experimental Total Bond	Kelauve error
		Group	Group									i		Energy (eV)	Energy (eV)	
1	Missensiferen		-	-	6		0	0	0	0	0	0	0	25.14934	25,107	-0.00168
500	Niconialic							. ~		-	c	0	0	37,30704	37.292	0,000,0
	Nitroculinic	•				2 0						-	-	17171.01	157 07	XC0000
	I-Nitropropanc		_	_	7	-	7	=	•	-	>	•	٠ د	110000		10000
	2. Mitronmonno	-	_	,			0	7	0	0	0	=	0	49.56563	49,602	F 000.0
	- Mindispan							•	0	c	0	0	0	61.62244	61,601	-0.00036
	1-Miroburanc			- •			, c				0	0	7	61.90697	61.945	0,00061
	Z-rvinoisconiane	-		•			,	= 4			. <			1.1001.1	72 750	20000
	I-Nitropentane	_	_	_	,	٥	4	=	=	<b>-</b>	-			13.10014	13.133	10,000

	θ. (		7 thane	J. J. thanc	_	8 E) 8 E)	(a) (a) (a)	auc)	$\neg$	7	-	8 1		Τ	(i)	g
	Exp. θ		IO7 (nitromethane	125,3 (nitromethane		(propane) 112 (propane) 113.8 (butane) 110.8						110.8	anoces .	FIII.4	(Isobutane)	(Isobutz
	Cal. θ		106.87	126,52	108.44	110.49	110,49		109.50	109,44	109.44	110.67	110,76	111.27	111.27	101
	ø, ⊙	:														
	e_ ©	:														
	θ, ©	:			_	69.51	69.51			70.56	70.56					23.50
	E ₇ (eV)		0	-1.44915	0				-			-1.85836	0	0	-1.85836	
om, mspAU).	25		0,99312	0.81549	1.15796			70231	1.000			0.81549	1.04887	1.04887	1.04887	
t (alom – al	<b>ਹ</b> ੋ		0.75	_	0.75			27.0				-	6.75	0.75	0.75	
SCU. LT IS I	2	-	-	-	-			_					_	_	-	
Bic welc u	ت		0.75	_	-			-	•			-	0.75	0.75	0.75	
e preceding an	C ₂ Alom 2		0.91140 (Eq. (15.116))	0.81549	-			_				0.81549	0.91771	0.91771	0.91771	
THE TRANSPORT	C ₂ . Atom 1		17716.0	0,81549	0.86359			0,86359				0.81549	0.87495	0.87495	0.87495	
The product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the product of the pr	Atom 2 Hybridization Designation	(Table 15.3.A)	z	24	π,			Æ				я	-	-	-	
	E Cantombre Atom 2		-14,53414	-16.68411	π			I			21,000		-14.82575 C,	-14.82575 C _a	-14.82575	
	Atom I Hybridization Designation	(Table 15.3.A)	<b>-</b> ,	24	7	~		7				R	3.	15	5	
⊢	Ecurlantre or E	Atons 1	-14.82575	-16.68411°	-15,75493			-15.75493			C11/89/31-	(,,	-15.55033 C_	-15.55033 C,	-15.55033 C ₄	
,	Zc' Terminal Atoms (a _b )		3.9665	4.1231	3.4252	ı		3.4252				4.7958	4.1633	4,1633	4.7958	
	2c' llosd 2 (a ₀ )		2,09711	2,30843	2.11106			2.09711				2.91547	2.11323	2.09711	2.90327	
	20' Bond 1 (a ₀ )		2.81279	2.30843	2.11106			2.09711				2.91547	2.91547	2.91547	2.90327	
Atoms of Amele			ZNC,H	40N_02	Methylana ZHC, H	"אנ"נ"	Н". Э".Э.	Mehyl ZHC H	7,7,7	H', J', 77	7.7.77	, " c iso (",	ZC,C,H in C,	ZC,C,H 120 C,	ادم لا "ر" ادم لا "	7C,C,C,

Table 15.194. The bond angle parameters of nitroalkanes and experimental values [1]. In the calculation of  $heta_r$ , the parameters from the preceding angle were used.  $E_r$  is  $E_r$  (arom

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## ALKYL NITRITES $(C_n H_{2n+2-m} (NO_2)_m, n = 1, 2, 3, 4, 5...\infty)$

The alkyl nitrites,  $C_n H_{2n+2-m} (NO_2)_m$ , comprise a RC-O-NO moiety that comprises C-O, O-N, and NO functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise 5 methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  3P_2 . The electron configuration of nitrogen is  $1s^2 2s^2 2p^3$ , and the orbital arrangement given by Eq. (10.134) has three unpaired electrons corresponding to the ground state  ${}^4S_{3/2}^0$ . The bonding in the nitro (NO) functional group is similar to that in the SO group given previously. It also has similarities to the bonding in the carbonyl functional group. In the NO group, the two unpaired electrons of the O atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the O-N functional group that is further energy matched to the  $C2sp^3$  HO of the C-O functional group. To meet the equipotential condition of the union of the  $N=O-H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.51) for the N=O-bond MO given by Eq. (15.140) is  $c_2(O \text{ to } N2p \text{ to } C2sp^3HO) = 0.85987$ .

As in the case of the carbonyl group, two unpaired O electrons result upon bond 25 breakage of the N=O bond which requires that two times  $E_{mag}$  of oxygen (Eq. (15.59)) be subtracted from the total energy of NO. Additionally,  $E_T(atom-atom, msp^3.AO)$  and  $\Delta E_{H_2MO}(AO/HO)$  are equal to -0.92918~eV (Eq. (14.513)) which matches the energy of the N=O bond with the contiguous O-N bond and matches the energy contribution of an oxygen atom.

The O-N functional group comprise a single-bond,  $H_2$ -type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the  $C2sp^3$  HO of the C-O functional group. In alkyl nitrites, the hybridization factor  $c_2$  of Eq. (15.52) for the C-O-bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO\ to\ O)=0.85395$ . The hybridization factor  $c_2$  of Eq. (15.52) for a C-N-bond MO given by Eq. (15.116) is  $c_2(C2sp^3HO\ to\ N)=0.91140$ . Thus, the hybridization factor  $c_2$  of Eq. (15.52) for O-N that bridges the C-O and N=O bonds given by Eq. (15.69) is

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727$$
 (15.141)

10  $E_r(atom-atom,msp^3|AO) = -0.92918 \ eV$  in order to match the energy of the NO group and  $E(AO/HO) = -15.35946 \ eV$  in order to match the C-O functional group.

The C-O functional group is equivalent to that of an ether as given in the corresponding section except that  $E_T(atom-atom,msp^3.AO)$  and  $\Delta E_{H_2MO}(AO/HO)$  are both -0.72457~eV which matches the energy contribution of an independent  $C2sp^3$  HO (Eq. 15 (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrites are given in Tables 20 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.79-15.108) are given in Table 15.200.

itrites.												
unctional groups of alkyl n Group Symbol	NO	N-0	0-0	$C-H\left(CH_3\right)$	$C-H\left(CH_{2}\right)$	H-)	('-(' (a)	() () ()	(c) (c)	(E) .))	(e) (c)	C-C (f)
Table 15.195. The symbols of functional groups of alkyl nitrites. Functional Group.	NO group	2-0	0.50	CH, group	CH ₂ group	E)	CC bond (n-C)	CC bond (iso-C)	CC bond (tert-C)	CC (iso to iso-C)	CC (t to t-C)	CC (t to iso-C)

Table 15.196. The peometrical bond parameters of alkyl nitrites and experimental values [1].

C-C (f)	2.10725	1.45164			1,53635	1	1.532	(propane)	1.531	(butane)	1.52750	00000
C-C(e) Group	2.10725	1,45164		-	1.53635		1.532	(propane)	1.531	(butane)	1.52750	000000
C-C (d) Group	2.12499	1.45744		000	1.54280		1.532	(propare)	1.531	(butane)	1.54616	0 50500
C – C (c) Group	2.10725	1.45164		1000	1,33033		1,532	(propane)	1.531	(butane)	1.52750	00000
C-C (b) Group	2,12499	1.45744		00170	1.34260		1,532	(propane)	1.531	(butane)	1.54616	0.68600
C – C (a) Group	2.12499	1,45744		00083 1	1.04400		1.532	(propane)	1.531	(butane)	1.54616	0 68600
C − H Group	1.67465	1.05661		1 11077	1.11047			1.122	(isobutane)		1.29924	0 63005
$C \sim H\left(CH_2\right)$	1.67122	1.05553		111713	2771111		1.107	(C~H propane)	1.117	(C~H butane)	1.29569	0.63159
$C \sim H\left(CH_{\lambda}\right)$	1.64920	1.04856		1 10974	1,701.1			(C-H propane)			1.27295	0.63580
dno ₂ O	1.85327	1,36135		1 44079				1.437	(methy) nitrate)		1,25751	0.73457
O-N Group	1.76440	1.32831		1 40587			1.402	(methy) nitrate)	764.1	(HNO,)	1.16134	0.75284
AO Group	1.32255	1.15002		1,21713		100.	507.1	(memyi ninate) (	7.1	(HWC),	0.65314	0.86955
Parameter	a (a ₀ )	$c'(a_n)$	Bond	Length	2c' (A)		Exp. Bond	Length	F	,	$h,c(a_0)$	C

Bond	Atom	E	12.	E	1	Final Total		7	Ecadons	E(C25m3)	θ,	θ	6	d,	d,
		(e)	(6)	(eV)	(e/)	Energy	(a)		.e.	(eV)	()	•	<u>`</u> ©	(a)	(a,)
		Bond 1	Bond 2	Bond 3	Bond 4	('2 <i>sp'</i>	Î	(3)	Final	Final	-			( )	\n_1
RON=O	0	-0.46439	D	0	0		000001	0.88983	-15.29034		137.15	42.85	06.79	0.49764	0.65238
RON=O	2	-0.46459	-0.46459	0	0		0.93084	0.86359	-15.75493		136.09	43.91	66.48	0.52781	0.62221
RO, - NO.	o	-0,46459	-0.36229	0	0		1.00000	0.86923	-15.65263	!	99.22	80.78	47.63	1.18905	0.13925
RO, - NO.	2	-0,46459	-0.46459	0	0		0.93084	0.86359	-15.75493		98.78	81.22	47.30	1.19655	0,13175
$RH_2C_u - O_bNO_a$ $R = H_1alkyl$	o [*]	-0.36229	-0 46459	0	0 -		1.00000	0.86923	-15,65263		91.43	88.57	43.71	1.33962	0.02173
H ₃ C _u - O _h NO _u	.,	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	93.71	86.29	45.31	1.30342	0,05793
-CH ₂ H ₂ C _" - O _h NO _"	ر. ' ا	-0.36239	-0 92918	9	0	-152.90716	17716.0	0.84418	-16.11722	-15.92636	89.16	90.84	42.16	1.37373	0.01238
('-H (CH ₃ )	i	-0.92918		G.	0	-152.54487	0.91771	0.86359	-15 75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
C-H (CH ₂ )	t	-0.92918	-0 92918	0	0	-153.47406	17216.0	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0,29933
C-H (CH)	t	-0.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0,77247	-17.61330	-17,42244	61.10	118.90	31.37	1,429%8	0.37326
$H_3C_aC_bH_2C_{ab}$	ن'	-0.92918	. 0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1,83879	0.38106
$H_3C_G'F_4T_3C_{H_2}$ – (C – C (a))	ڻ	-0.92918	-0.92918	0	0	-153,47406	0,91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	06806'1	0,45117
$R - H_2(', C_k(H_2(', -R')H(H_2 - (C - C; (b))))$	<u>ೆ</u>	-0.92918	-0.92918	-0.92918	0	-154,40324	0,91771	0.77247	-17.61330	-17,42244	48.30	131.70	21.90	1,97162	0.51388
$R - H_2C_a(R' - H_2C_a)C_A(R'' - H_2C_a)C'H_2 - (C' - C'(c))$	ڻ'	-0,92918	-0.72457	-0,72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$ixo(C_{\mu}C_{\mu}(H_{2}C_{\mu}-R))HCH_{2} (C-C_{\mu}(d))$	, C,	-0.92918	-0.92918	-0.92918	0	-154.40324	0,91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$ter(C_{*}(R^{1}-H_{2}C_{*})C_{*}(R^{2}-H_{2}C_{*})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-C^{2})CH_{2}-(C^{2}-$	ڻ	-0,72457	-0,72457	-0.72457	-0.72457	-154.51399	0.91771	0.76763	-17,92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$ler(C,C,\{H_2C,-R^1\}HC,H_2-\{C^2,C^2\})$	C,	-0,72457	-0.92918	-0.92918	49	-154,19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$iso("_{*}(R-H_{2}C_{*})C_{*}(R"-H_{2}C_{*})CH_{2}-$	ť	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.76765	-17,92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.197. The MO to HO intercept geometrical band parameters of alkyl nitrites. R, R', R" are H or alkyl groups. E_T is E_T (atom - atom, msp², AO).

-	ON	N - 0	0-0	(.H ₃	CH ₂	C-#	$\widetilde{C} = C$ (a)	C-C (p)	(e) U-C	(e) U-U	() (c)	(t) 2-2
	dionib	dioio	dnoso	Group	Group	Group	Group	Group	Group	Group	Group	Group
n,	2	_	1	EO.	2	-	11	_	_	-	1	-
n,	0	0	0	2	-	0	0	0	0	0	0	o
$n_{j}$	0	0	0	0	0	0	0	0	0	0	c	c
ζ,	5.0	0.5	0.5	0.75	0.75	0.75	0.5	0,5	0.5	0.5	0.5	0.50
C ₂	-	1	1		-	1	_	_	1	-	-	-
$c_1$	1	_	-	_	-	_	-	-	_			-
C,	0.85987	1.06727	0.85395	0.91771	17/16.0	17716.0	0.91771	17716.0	0.91771	17716.0	17716	17710
ς,	2	0	0	0	1	-	0	0	0	_	1-	0
د'،	4	2	2	1		-	2	2	2	2	2	2
ć,	0	0	0	3	2	_	0	0	0	0	0	0
	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
23	-	1	-	1	1	_	1	1	1	1	-	-
V, (eV)	-108.34117	-42.83043	-32.04173	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_{r}(eV)$	23.66182	20.48593	9,99436	38.92728	25.78002	12.87680	9,33352	9.33352	9.37273	9.33352	9.37273	9.37273
" (eV)	40.95920	12.13739	8.64465	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V, (eV)	-20.47960	-6.06870	-4.32232	-16.26957	-10.53337	-5.24291	-3.38732	-3,38732	-3.45250	-3,38732	-3.45250	-3,45250
E(*v m) (eV)	0	-15.35946	-14.63489	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{n_1 1 1 0}$ [. so no) (eV)	-0.92918	0	-0.72457	0	0	0	0	0	0	0	0	0
$E_{\tau}(\omega m)$ (eV)	0.92918	-15.35946	-13.91032	-15.56407	-15.56407	-14.63489	-15,56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(n_2m)$ (eV)	-63.27057	-31.63527	-31,63537	-67.69451	-49.66493	-31,63533	-31.63537	-31,63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{\tau}(atom - atom, msp^3, AO)$ (eV)	-0.92918	-0.92918	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T[sto]$ (eV)	-64.19992	-32.56455	-32.35994	-67.69450	-49.66493	-31.63537	-33.49373	-33,49373	-33.08452	-33.49373	-33.08452	-33.08452
w (10 ¹⁵ rad / s)	19.2199	23.3578	20.7301	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9,55643	9.55643
$E_{\kappa}$ (eV)	12,65089	15.37450	13.64490	16.40846	15.97831	15.91299	6,21159	6.21159	10.19220	6.21159	6.29021	6.29021
$E_{\mu}$ (eV)	-0.22587	0.25261	-0.23648	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{Kab}$ (eV)	0.20396 [46]	0.10725	0.13663	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0,12312 [2]	0.17978	0.09944	0.12312	0.12312	0.12312
$E_{\rm uc}$ (eV)	-0.12390	0.19899	-0.16817	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E sep (eV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\gamma}$ (chap) $(eV)$	-64.44771	32.76354	-32.52811	-67.92207	-49,80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E mind (c, . 10 110) (cV)	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14,63489
Eman (c, w 110) (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
E 11 (Time) (CV)	5.67933	3,49376	3.25833	12.49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

C-C (f) C-C (d) C-C (e) Table 15.199. The total bond energies of alkyl nitrites calculated using the functional group composition and the energies of Table 15.198 compared to the experimental values [3].

Formula

Name NO O - N C - O  $CH_3$   $CH_4$   $CH_5$   $CH_5$  C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C - C C

	$\Gamma$					т	T	т—	_		т				
	Exp. θ	€		110.7	107	(propane) 113.8 113.8 (butane) 110.8 freshmane)	(butane)	(isonatianica)			110.8 (isobutanc)		111.4 (isobutane)	111.4 (isobutanc)	
	Cal. 9	€ —	113.33	112.38	108.44	110.49	110.49	109.50	109,44	109,44	110,67	110.76	111.27	111.27	
	9,	©	1	L											T
	9	<u> </u>													T
	6	<u> </u>	_	_	_	15.00	69.51		70.56	70.56					ę
	E	(e _V )	-1.44915	-1.449[5	0			0			-1.85836	c	0	-1.85836	
om, msp3.AO	200		0.86345	0.81549	1.15796			1.15796			0.81549	1.04887	1.04887	1.04887	
$E_T(atom-at$	·5-		-	_	6,75			0.75				0.75	0.75	6.75	
sed. $E_T$ is $I$	ڻ		_	_	-		1=	-					-	_	
ngle were u	ڻ		_	_	_			_			_	0.75	0.75	0.75	
e preceding a	ال بي	7 1000	0.91140 (Eq. (15.116))	0.81549	- ,			_			0.81549	0.91771	0.91771	0.91771	
meters from th	C ₂		0.81549	0.81549	0,86359			0,86359			0.81549	0.87495	0,87495	0.87495	
tion of $\theta_{\tt r}$ , the para	Atom 2 Hybridization	Designation (Table 15.3.A)	N.	24	H			н			25	_	-	_	
n the calcula	Eranioning Atom 2		-14,53414 N	-16.68411 O,	Ŧ			н			-16.68412 C	-14.82575 C,	-14.82575	-14.82575 C.	
cental values [1].	Atom i Hybridization	Designation (Table 15.3.A)	25	저	7			7			25	35	ş	ş	
and experim	E Combather	E Atom I	-16.68412 C,	-16,68411	-15,75493			-15.75493			-16.68412	-15.55033	-15.55033	-15.55033 C.	
alkyt nttrite	2c' Teminal	Atmax ( a ₀ )	4,4944	4,1231	3,4252			3.4252			4.7958	4.1633	4.1633	4.7958	
rameters of	2c'   Bend 2	(a _n )	2.63661	2.65661	2.11106			2.09711			2.91547	2.11323	2.09711	2.90327	
ond angle pa	2c' Bond 1	(a _n )	2.72270	2,30004	2.11106			2.09711			2.91547	2.91547	2.91547	2.90527	
table 15.200. He comed angle parameters of alkyl nurroes and experimental values [1]. In the calculation of 0, the parameters from the preceding angle were used. E, is E, (ann.—atom, msp², AO)	Albais en Angle		ACO,N	400,00	Methylana ZHC, H	דנ."נ"נ	H*.5".77	H" ZHZ	ֿלנ"נ.'נ.' לנ"ניינ	H", J", J7	יים נ" דנ"נ"נ"	AC;C,H 150 C.	ابه در" H*ک*.)7	ומו כ." ע"ל."נ."	7,7,7,17

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ALKYL NITRITES 
$$(C_n H_{2n+2-m} (NO_2)_m, n = 1, 2, 3, 4, 5...\infty)$$

The alkyl nitrites,  $C_nH_{2n+2-m}(NO_2)_m$ , comprise a RC-O-NO moiety that comprises C-O, O-N, and NO functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise 5 methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2CH)$  and t-butyl  $((CH_3)_3C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  3P_2 . The electron configuration of nitrogen is  $1s^2 2s^2 2p^3$ , and the orbital arrangement given by Eq. (10.134) has 15 three unpaired electrons corresponding to the ground state  ${}^4S_{3/2}^0$ . The bonding in the nitro (NO) functional group is similar to that in the SO group given previously. It also has similarities to the bonding in the carbonyl functional group. In the NO group, the two unpaired electrons of the O atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the O-N functional group that is further energy matched to the  $C2sp^3$  HO of the C-O functional group. To meet the equipotential condition of the union of the  $N=O-H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.51) for the N=O-bond MO given by Eq. (15.140) is  $c_2(O to N2p to C2sp^3HO) = 0.85987$ .

As in the case of the carbonyl group, two unpaired O electrons result upon bond 25 breakage of the N=O bond which requires that two times  $E_{mag}$  of oxygen (Eq. (15.59)) be subtracted from the total energy of NO. Additionally,  $E_T \left( atom-atom, msp^3.AO \right)$  and  $\Delta E_{H_2MO} \left( AO / HO \right)$  are equal to  $-0.92918 \, eV$  (Eq. (14.513)) which matches the energy of the N=O bond with the contiguous O-N bond and matches the energy contribution of an oxygen atom.

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The O-N functional group comprise a single-bond,  $H_2$ -type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the  $C2sp^3$  HO of the C-O functional group. In alkyl nitrites, the hybridization factor  $c_2$  of Eq. (15.52) for the C-O-bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO\ to\ O)=0.85395$ . The hybridization factor  $c_2$  of Eq. (15.52) for a C-N-bond MO given by Eq. (15.116) is  $c_2(C2sp^3HO\ to\ N)=0.91140$ . Thus, the hybridization factor  $c_2$  of Eq. (15.52) for O-N that bridges the C-O and N=O bonds given by Eq. (15.69) is

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727$$
 (15.141)

 $E_T(atom-atom, msp^3.AO) = -0.92918 \ eV$  in order to match the energy of the NO group and  $E(AO/HO) = -15.35946 \ eV$  in order to match the C-O functional group.

The C-O functional group is equivalent to that of an ether as given in the corresponding section except that  $E_T(atom-atom,msp^3.AO)$  and  $\Delta E_{H_2MO}(AO/HO)$  are both -0.72457~eV which matches the energy contribution of an independent  $C2sp^3$  HO (Eq. 15 (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrites are given in Tables 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.79-15.108) are given in Table 15.200.

Table 15,195. The symbols of functional groups of alkyl nitries. Functional Group	CN	N-0	0-3	$C-H\left\{ (TH_3)\right\}$	$C \sim H\left(CH_{\frac{1}{2}}\right)$	H-J	('~('a)	(q) .)-,)	(a) (b - 1)	色してし	(-(j (e)	(,-(,()
Table 15.195. The symbols Functional Group	NO group	N.O	9	CH ₃ group	CH, group	Đ	CC bond (n-C)	CC bond (iso-C)	CC bond (tert-C)	CC (iso to iso-C)	CC (tro t-C)	CC (t to iso-C)

Table 15,196. The geometrical bond parameters of ally! nitrites and experimental values [1].

(f) 2-2	Group	2.10725	1.45164	1.53635	1,532 (propane) 1,531	1.52750	
(e) 2~2	Group	2.10725	1.45164	1.53635	1.532 (propane) 1.531 (hutane)	1.52750	0 00000
C-C (d)	Group	2.12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	20000
(a) 2-2	Group	2,10725	1,45164	1.53635	1,532 (propane) 1,531 (butane)	1.52750	000000
(q) 2-2	Group	2,12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	00,00,0
C - C (a)	Group	2.12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	000000
C~H	Group	1.67465	1.05661	1.11827	1.122 (isobutane)	1,29924	0 62006
$C \sim H(CH_2)$	Group	1.67122	1.05553	1.11713	1.107 (C-H propane) 1.117 (C-H butane)	1.29569	0.42150
$C-H(CH_3)$	Group	1.64920	1,04856	1,10974	1.107 (C - H propane) (C - 1.117 (C - H butane) (C -		085290
0-0	Group	1.85327	(,36135	1,44079	1.437 (methyl nitrate)	1,25751	0 72457
N-0	Group	1.76440	1,32831	1,40582	1.402 (methyl nitrate) 1.432 ( HNO ₂ )	) (	0.75284
ON	Group	1.32255	1.15002	1.21713	d (methyl nitrate) 1,2 (HNO ₂ )	0,65314	0.86955
Parameter		a (a ₁ )	$c'(\sigma_o)$	Bond Length 2c' (A)	Exp. Bond Length (A)	$h_i c \left(a_o\right)$	

Bond	Atom	E	F _T	ET	ĒŢ	Final Total	, manal	Filast	Ecasions	$E(C2sp^3)$	.θ	θ	9	ď	d,
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	$(72xp^3)$	(a _o )	(a _p )	(eV) Final	(eV) Final	<u></u>	0	(C)	(a)	(a,)
RON = O	0	-0,46459	0	0	0		000001	0.88983	-15.29034		137 15	28 CP	67.00	P320F0	0.65729
RON = O	ν	-0.46459	-0.46459	0	0		0.93084	0.86359	-15.75493		(36,09	43.91	66.48	0.52781	0.0228
RO, - NO.	10	-0,46459	-0,36229	0	0		1.00000	0.86923	-15.65263		99.22	80.78	47.63	1.18905	0,13925
RO, -NO.	Ν	-0.46459	-0.46459	0	0		0.93084	0.86359	-15,75493		98.78	81.22	47.30	1.19655	0.13175
$RH_{2}C_{u} - O_{h}NO_{u}$ $R = H, alkyl$	10	-0.36229	654940-	O	0		1.00000	0.86923	-15,65263		91.45	88.57	43.71	1.33962	0,02173
$H_3C_a - O_bNO_a$	ن.'	-0.36229	0	0	٥	151.97798	0.91771	0.89582	-15.18804	-14.99717	93.71	86.29	45.31	1.30342	0.05793
$-CH_2H_2C_{,\prime}-O_{,\prime}NO_{,\prime}$	نْ	-0.36229	-0 92918	0	0	-152.90716	17716.0	0.84418	-16.11722	-15.92636	89.16	90.84	42.16	137375	0.01238
$C - H\left(CH_{\lambda}\right)$	ij	-0.92918	0	0	0	-152.54487	17716.0	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\left(CH_{2}\right)$	ر.	-0.92918	-0.92918	0	0	-153.47406	17716.0	0.81549	-16.68412	-16,49325	68.47	111.53	35.84	1.35486	0,29933
C-H (CH)	ر.	-0.92918	-0.92918	41626.0-	0	-154,40324	0.91771	0,77247	-17,61330	-17.42244	61,10	118.90	31.37	1.42988	0.37326
$H_3C_{\mu}C_{\mu}H_2CH_2 - (C - C_{\mu}C_{\mu})$	".)	816Z6'D-	0	0	0	-152.54487	17716.0	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_2(C_\mu C_\mu H_2 C H_2 - (C_\mu - C_\mu C_3))$	ر: ا	-0.92918	-0 92918	0	0	-153.47406	0,91771	0.81549	-16.68412	-16,49325	56.41	123.59	26.06	1,90890	0.45117
$R - H_2 C_{\mu} C_{\nu} \left( H_2 C_{\nu} - R^{\nu} \right) H C H_2 - (C - C^{\nu}(b))$	ر,	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2 C_a (R^- + H_2 C_J) C_b (R^0 - H_2 C_c) C H_2 - (C^ C^- C_0)$	ر,	-0.92918	-0.72457	-0.72457	-0,72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	62.181	21.74	1.95734	0.50570
$knC'.C_c + R' HCH_2 - (C-C' G)$	ن'	-0.92918	-0.92918	-0.92918	0	-154.40324	17716.0	0.77247	-17.61330	-17.42244	48,30	131.70	21.90	1.97162	0.51388
$ler(C_{\mu}(R-H_2C_{\mu})C_{\mu}(R^{n}-H_2C_{\nu})CH_2-(C-C_{\nu}(0))$	۲.)	-0.72457	-0.72457	-0,72457	-0.72457	-154,51399	17716.0	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$ler(C',C',K(H_2C,-R')HCH_2-(C'-C',f))$	ڻ	-0.72457	-0.92918	-0.92918	đ	-154.19863	0.91771	0.78155	-17,40869	-17.21783	32.78	127.22	24.04	1.92443	0.47279
$ksoC_{a}(R^{*}-H_{2}C_{a})C_{a}(R^{*}-H_{2}C_{c})CH_{2}-$ (C; -C; (f))	۲,	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	17716.0	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.197. The MO to HO intercept geometrical band parameters of alkyl nitrites. R, R', R'' are H or alkyl groups.  $E_T$  is  $E_T(atom-atom, mxp^2, AO)$ .

Parameters	NO Group	dno.D Q-O	Parameters $N(r) O - N C - O$ Group Group Group	C'H ₃ Group	CH ₂ Group	C-H Group	C − C (a) Group	C C (b) Group	C – C (c) Group	CーC (d) Group	C-C (e) Group	C - C (f) Group
$n_{\rm f}$	2	_	1		2	-		_	_	_	_	-
'n,	0	0	0	2	J	0	0	0	0	0	0	0
, n ₃ ,	0	0	0	0	0	0	0	0	0	0	0	0
C.	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
۲.	1	ı	_	1	_	121	_	-		-	-	-
c,	1	1	1	1	_	1	1	_	1	_		-
ر.	0.85987	1.06727	0.85395	17716.0	0.91771	0.91771	0.91771	17716.0	17716.0	0.91771	0.91771	17716.0
c,	2	0	0	0	1	1	0	0	0	_	1	0
c,	4	2	2	1	1	1	2	2	2	2	2	2
C,s	0	0	0	m	2	1	0	0	0	0	0	0
·.'	0,5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	6.5	0.5
(3,	ı	-	1	1	-	-	1	1	1	. 1	1004	_
V, (eV)	-108.34117	-42.83043	-32.04173	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_r$ (eV)	23.66182	20.48593	9.99436	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T(aV)	40.95920	12.13739	8.64465	32,53914	21.06675	10,48582	6,77464	6.77464	6.90500	6.77464	6.90500	6.90500
V (eV)	-20.47960	-6.06870	-4.32232	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3,45250	-3.38732	-3.45250	-3.45250
E(20 110) (eV)	0	-15.35946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{n_1 n n}$ (so no) (eV)	-0.92918	0	-0.72457	0	0	0	0	0	0	0	0	0
$E_{\tau}(\omega m) (eV)$	0.92918	-15,35946	-13.91032	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(u_2 m)$ (eV)	-63.27057	-31.63527	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31,63535	-31,63537	-31.63535	-31,63535
$E_T(atom - atom, nisp^3, AO)$ (eV)	-0.92918	-0.92918	-0.72457	0	0	0	-1.85836	-1.85836	51644:1-	-1.85836	-1.44915	-1.44915
$E_T(\omega)$ (eV)	-64.19992	-32.56455	-32.35994	-67.69450	-49,66493	-31.63537	-33,49373	-33,49373	-33.08452	-33.49373	-33.08452	-33,08452
$\omega \left(10^{18} rad Is\right)$	19,2199	23.3578	20,7301	24.9286	24.2751	24.1759	9,43699	9.43699	15,4846	9,43699	9.55643	9.55643
$E_{k}$ $(eV)$	12.65089	15.37450	13.64490	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\vec{E}_{p}$ (eV)	-0.22587	0.25261	-0.23648	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$ec{E}_{Kab}$ (eV)	0.203% [46]	0.10725 f471	0.13663	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312	0.17978	0.09944	0,12312	0.12312	0.12312
$\vec{E}_{mc}$ (eV)	-0.12390	0.19899	-0.16817	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{meg}$ (eV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(u_{nep})$ (eV)	-64,44771	32,76354	-32.52811	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33,59732	-33.18712	-33.18712
Emme (c. so no) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Exerted (cz. 10) (eV)	0	0	0	-13,59844	-13,59844	-13.59844	0	0	0	0	0	0
$E_{\mu}(c_{map})$ $(aV)$	5.67933	3.49376	3,25833	12.49186	7.83016	3,32601	4.32754	4.29921	3,97398	4.17951	3.62128	3.91734

C-C (I) C-C (q) C-C (e) Table 15.199. The total bond energies of alkyl nitrites calculated using the functional group composition and the energies of Table 15.198 compared to the experimental values [3].

Formula None NO O-N C-O CH; CH; CH C-C (a) C-C (b) C-C (c)

Group Group Group

				.,	,						,			
	Exp. <i>θ</i>		110.7 (HNO,)	107 (propane)	112 (propane) 113.8 (butane) 110.8 (sobutane)	111.0 (bulane) 111.4 (Isobutane)				110.8 (isobutane)		111.4 (isobutane)	111.4 (isobutane)	
	(°)	113.33	112.38	108.44	110.49	110.49	109.50	109.44	109.44	110.67	110.76	111.27	111.27	107.50
	(9)													
	(0)													
	(6)				69,51	15.09		70.56	70.56					72.50
	E ₇ (eV)	-1.44915	-1,44915	0			0			-1.85836	0	0	-1,85836	
om, $msp^3$ . $AO$	5	0.86345	0,81549	1.15796			1.15796			0.81549	1.04887	1.048%7	1.04887	
$z_T (atom - at)$	<b>5</b>	-	-	0.75	-		0.75	-		-	0.75	0.75	0.75	
sed. $E_T$ is $I$	ڻ س	-	· <b>-</b>	-	-		-			_	_	-	-	
ngle were us	ىت		-	-			_			_	0.75	0.75	0.75	
e preceding a	C ₂ Alon 2	0.91140 (Eq. (15.116))	0.81549				1			0.81549	17716.0	17116.0	0.91771	
neters from th	C ₂ Atom 1	0.81549	0.81549	0.86359			0.86359			0.81549	0.87495	0.87495	0.87495	
values [1]. In the calculation of $ heta_r$ , the parameters from the preceding angle were used. $E_r$ is $E_r(atom-atom,msp^i.AO)$	Atom 2 Hybridization Designation (Table 15.3.A)	z	24	π			Н			25		-	1	
n the calcula	E Contembre Alons 2	-14,534[4 N	-16.68411 O _b	н			π			-16,68412 C;	-14.82575 C,	14.82575	-14.82575 C.	
ental values [1]. 1	Atom I Hybridization Designation (Table 15.3.A)	22	24	7			7			. 22	ş		ş	
and experim	E Contante Or E Atom 1	-16,68412 C,	-16.68411 O	-15.75493	N.	. ,	-15.75493			-16,68412 (*,	-15.55033 C.	(,	-15,55033	
alkyl nitrites	2c' Terminal Atoms ( a _n )	4,4944	4.1231	3.4252			3.4252			4.7958	4.1633	4 1633	4,7958	
rameters of	2c' Bend 2 (a ₀ )	2,65661	2.65661	2,11106			2.09711			2.91547	2.11323	2.09711	2.90327	
nd angle par	. 2c' Band I (a ₀ )	2,72270	2,30004	2.11106			2.09711			2.91547	2.91547	2.91547	2.90327	
Table 15.200. The bond angle parameters of alkyl nitrites and experimental	· Awas af Angie	N*OJ7	40N°07	Methydenu ZHC "H	אב"ב"נ"ב	H, J, JZ	H."ZHZ	حر"ر.۴ر.	H".)".)7	۵۰ ر" حزر در د	ZC,C,H isa C,	∠C'_C'H i∞ C'_	ומו נ." קנ"לנ"נ"	".)".)Z

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ALKYL NITRATES 
$$(C_n H_{2n+2-m} (NO_2)_m, n = 1, 2, 3, 4, 5...\infty)$$

The alkyl nitrates,  $C_n H_{2n+2-m} (NO_3)_m$ , comprise a  $RC-O-NO_2$  moiety that comprises C-O, O-N, and  $NO_2$  functional groups. The alkyl portion of the alkyl nitrate may comprise 5 at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrates are equivalent to those in branched-chain alkanes.

The  $NO_2$  functional group is equivalent to that of nitro alkanes with the exception that  $\Delta E_{H_2MO} \left(AO/HO\right)$  as well as  $E_T \left(atom-atom,msp^3.AO\right)$  is equal to -3.71673~eV in order to match the group energy to that of the contiguous O-N bond. Furthermore, the O-N group with  $E_T \left(atom-atom,msp^3.AO\right) = -0.92918~eV$  is equivalent to that of nitrites as given in the corresponding section.

The C-O functional group is equivalent to that of an ether as given in the corresponding section except that  $E_T(atom-atom,msp^3.AO)$  and  $\Delta E_{H_2MO}(AO/HO)$  are both 20 -0.92918 eV which matches the energy contribution of an independent  $C2sp^3$  HO (Eq. (14.513)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrate.

The symbols of the functional groups of branched-chain alkyl nitrates are given in Table 15.201. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrates are given in Tables 15.202, 15.203, and 15.204, respectively. The total energy of each alkyl nitrate given in Table 15.205 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.204 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrates determined using Eqs. (15.79-15.108) are given in Table 15.206.

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Table 13.201. The symbols o	Table 13,201. The symbols of functional groups of alkyl nitrates.
Functional Group	Group Symbol
NO ₂ group	NO,
N-0	, N - O
0-0	: 0-0
CH, group	$C-H\left(CH_3\right)$
CH ₂ group	$(C-H (CH_1))$
СН	( H - )
CC bond (n-C)	(3)
CC bond (iso-C)	( <del>)</del>
CC bond (tert-C)	(a) (b) (c)
CC (iso to iso-C)	(E) U-U
CC (t to t-C)	(=) (=)
CC (t to iso-C)	€ 5-3

rarameter	2/2	~	7	Parameter NO C N								
.	Group	Group	Group	$C - H \left( CH_3 \right)$ Group	$C-H(CH_1)$ Groun	C – H Group	C – C (a) Group	- C-C (b) Group	C – C (e) Group	C-C (d) Group	C-C (e)	(J) (J)
	1.29538	1.76440	1.83991	1.64920	1.67122	1.67465	2 12499	2 12/400	30201.0	1	d de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de la companya de l	dnoio
	1.13815	1,32831	1.35643	1 04856	1 05563	1 0000		2.12.77	2.101.2	7.12499	2.10725	2.10725
T					CCCCO.1	1.03661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
	1.20456	1.40582	1.43559	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exn Bond	1.205	1.402		1 107	200							
Length (A)	(methyl nitrate) 1.2 (HNO ₂ )	(methyl nitrate) 1.432 (HNO ₂ )	1.437 (methyl nitrate)	(C-H  propane) $1.117$ $(C-H  butane)$	(C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531	1.532 (propane) 1.531	1.532 (propane) 1.531	1.532 (propane) 1.531	1.532 (propane) 1.531	1.532 (propane) 1.531
h c (a)	0.61857	1 15174	0,0,0				(ontaile)	(ontane)	(butane)	(butane)	(butane)	(butane)
+	0.0100	1.101.34	1,24512	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1 54616	1 57750	1 57750
$\forall$	0.8/862	0.75284	0.73723	0.63580	0.63159	0,63095	0.68600	0.68600	0.68888	000000	001201	00/701

Table 15.203. The MO to HO intercept geometrical bond parameters of alkyl nitrates. $R,R',R''$ are $H$ or alkyl groups.	netrical bo	nd parameters of	falkyl nitrates. In	R, R', R" are H (	or alkyi groups.	$E_{r}$ is $E_{r}(aton$	$E_r$ is $E_T(atom - atom, msp^3.AO)$	40).							
Bond	Atom	F _T	E.	F.	E	Final Total	, mind	, m	Eratoso	E[C2sp3]	θ.	θ,	θ,	d,	d,
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy ('2 <i>sp</i> ') (eV)	(a ₀ )	(0)	(eV) Final	(eV) Final	0	· (c)	E	(a,)	(a°)
RN(O) = O	0	-0.92918	0	0	0		1 00000	0.86359	-15.75493		138.49	41.51	07.79	0.49144	0,64671
RN(O) = O	2	-0.92918	-0.92918	-0,46459	o,		0,93084	0.79340	-17.14870		135,60	44.40	63.83	0.57133	0,56682
$RO_h - N(O_a)_2$	O ⁴	-0.46439	-0,46459	0	0		1.00000	0,86359	-15,75493		98.78	81.22	47.30	1.19635	0.13175
$RO_b - N(O_a)_2$	×	-0.46439	-0.92918	-0.92918	c		0.93084	0.79340	-17.14870		92.78	87,22	43.03	1,28978	0.03852
$RH_2C_n - O_hN(O_n)_2$ $R = H, alkyl$	ర	-0.46439	-0,46459	0	0		1,00000	0.86359	-15.75493		92.13	87.87	43.96	1.32431	0.03212
$H_3C_a - O_bN(O_a)_2$	ر"	-0.46459	0	c	•	-152.08028	17716,0	0.88983	-15.29034	-15.09948	94.36	85.64	45,54	1,28872	0.06771
$-CH_1H_1C_2-O_6N(O_2)_2$	ڻ	-0.46459	-0.92918	0	D	-153,00946	17716.0	0.83885	-16.21952	-16.02866	89.90	90.10	42.44	1.35787	0,00143
$C-H$ $(CH_3)$	Ü	-0.92918	0	Ð	ç	-(52.54487	17416.0	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1,23564	0.18708
(C-H (CH ₂ )	i	-0.92918	-0.92918	c	0	-153.47406	12716.0	0,81549	-16.68412	-16,49325	68.47	111.53	35.84	1.35486	0.29933
C-H (CH)		-0.92918	-0.92918	-0.92918	0	-154.40324	17716.0	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_1C_nC_nH_2CH_2 - (C_nC_nC_nC_nC_nC_nC_nC_nC_nC_nC_nC_nC_nC$	".	-0.92918	0	0	0	-152.54487	12216.0	0.86359	-15.75493	-15,56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2^2H_3$ — (C'-C' (a))	ئ	-0.92918	-0.92918	0	0	-153.47406	17716.0	0,8[549	-16 68412	-16,49325	56.41	123.59	26.06	06806:1	0,45117
$R - H_2C_A(H_2C_a - R)HCH_2 - (C - C'(b))$	ڻ'	-0.92918	-0.92918	81626'0-	0	-154,40324	17716.0	0.77247	-17.61330	-17,42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2 C_a (R' - H_2 C_a) C_b (R'' - H_2 C_a) C'_b (R'' - H_2 C_a) C'_b (R'' - H_2 C_a)$	ئ	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	17716.0	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$lsoC_aC_b(H_2C_c-R^b)HCH_2-$ (C'-C' (d))	ڻ	-0.92918	-0.92918	-0.92918	0	-154,40324	17716.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$ler(C_{\sigma}(R-H_2C_{\sigma})C_{\sigma}(R^{-}+H_2C_{\sigma})CH_2-(C-C^{-}(e))$	ر؛	-0,72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$leiK'_{G'_{k}}(H_{2}C_{s}-R')HCH_{2}-(C-C'_{s}(f))$	, C,	-0.72457	-0.92918	-0.92918	9	-154.19863	17710	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$ksoC_{\sigma}(R^{*-}H_{2}C_{\sigma})C_{\kappa}(R^{*-}H_{2}C_{\sigma})CH_{2} - CC_{\sigma}(R)$	: °	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129,96	22.66	1.94462	0.49298

raraneters	Oroup	Oroup	Gramb Gramb	Group	Group	Group	Group	Group	Group	Group	Group	Group
n,	2				2	-	~	-	-	-	-	-
n,	0	0	0	2	-	0	0	0	0	0	ø	0
H,	0	0	0	0	0	0 .	0	0	0	0	0	0
	6.5	5.0	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
	,~-				-	-		1	-	-	-	-
	-	-	_	_	_	_	-	-	_	-	-	-
7	0.85987	1.06727	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	17710	0.91771	17716,0
	0	0	0	0		_ 	0	0	0	-	-	0
	4	2	2	-	-	_	2	2	2	2	7	7
	0	0	0	3	2	_	0	0	0	0	0	0
4	0.5	0.5	0.5	0.75	0.75	0.75	6.5	0.5	0.5	0.5	0.5	6.5
a i	-	-	1	1	1	1	-	ş-	1	-	-	-
V, (eV)	-112,63415	-42.83043	-32,35681	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	23.90868	20.48593	10.03058	38.92728	25.78002	12.87680	9,33352	9,33352	9.37273	9.33352	9.37273	9,37273
T' (eV)	43.47534	12.13739	8.79304	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77454	6.90500	6.90500
V, (eV)	-21.73767	-6.06870	-4.39652	-16,26957	-10.53337	-5.24291	-3.38732	-3.38732	-3,45250	-3.38732	-3.45250	-3.45250
El.vo no) (eV)	0	-15.35946	-14.63489	-15.56407	-15.56407	-14.63489	-15,56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
DE uzaco (so not (eV)	-3.71673	0	-0.92918	0	0		0	0	0	0	0	0
$E_{r}$ (no no) (eV)	3,71673	-15,35946	-13.70571	-15.56407	-15.56407	-14,63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
$E_T(\mu_1 xr) (eV)$	-63.27107	-31.63527	-31.63542	-67.69451	-49,66493	-31.63533	-31,63537	-31,63537	-31,63535	-31.63537	-31.63535	-31.63535
$E_{\tau}(atom - atom, msp^{\dagger}.AO)$ (eV)	-3.71673	-0.92918	-0.92918	0	0	0	-1.85836	-1.85836	-1.44915	~1.85836	-1.44915	-1.44915
$E_{\gamma}(\iota \kappa)$ (eV)	-66.98746	-32.56455	-32.56455	-67.69450	-49,66493	-31.63537	-33.49373	-33,49373	-33.08452	-33.49373	-33.08452	-33.08452
w (1013 rad /s)	19.8278	23.3578	21.0910	24.9286	24.2751	24.1759	9.43699	9,43699	15.4846	9.43699	9.55643	9.55643
$E_{\kappa}$ (eV)	13.05099	15.37450	13,88249	16.40846	15.97831	15,91299	6.21159	6.21159	10.19220	621159	6.29021	6.29021
$\vec{E}_{o}$ (eV)	-0.23938	0.25261	-0.24004	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{k}_{\chi_{\mathrm{orb}}}$ (eV)	0.19342	0.10725 [47]	0.13663	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	(Eq. (13.458))	0.12312 [2]	0.17978	0.09944	0.12312	0.12312	0.12312
$\overline{E}_{out}(eV)$	-0.14267	0,19899	-0.17172	-0,22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{ m max}\left( cV ight)$ .	0,11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Er (timp) (eV)	-67.27281	32.76354	-32.73627	-67.92207	49,80996	-31,70737	-33.59732	-33.49373	-33,24376	-33.59732	-33.18712	-33.18712
E unted (2, 40 190) (eV)	-14,63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489
E mind (c. 10 10) (eV)	0	0	0	-13,59844	-13,59844	-13.59844	0	0	0	0	0	0
E. linger (eV)	8.73325	3,49376	3,46649	12,49186	2,83016	3,32601	4,32754	4.29921	3,97398	4.17951	3.62128	3.91734

C~C (e) Table 15.205. The total bond energies of alkyl intrates calculated using the functional group composition and the energies of Table 15.204 compared to the experimental values [3].

Formula Nanc  $NO_2$  O-N C-O  $(H_2$   $CH_2$   $CH_3$  C+C (a) C-C (b) C-C (b) C-C (c) C-C (d) Group Group

values [1], in the calculation of $\theta_s$ , the parameters from the preceding angle were used. $E_s$ is $E_s$ ( $abs$ ).  Atoms 2 $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$ $C_s$	0 95601 0 95801 1 1	70.36 109.44 (methyl nitrate)	0.75 1 0.75 0.93052 0 100.68	1 0.81549 -1,44915	15.09 115.09 118.1 (Red. (15.59)) (methyd nitrate)	<u> </u>	1 1 0.86345 -1.44915	1 1 0.75 1.15796 0 108.44	(400) (593) (593) (604) (604) (10.8 (10.8) (10.8) (10.8)	(thing) (110.49 (things) (10.49 (technine)	1 1 0.75 1.15796 0 16950	10.36	105.44	49 1 1 0.81549 -1.85836 110.67 (inchusine)	71 0,75 1 0,75 1,04887 0	71 0.75 i 0.75 1.04887 0 111.27 (Gobulane)	71 0.75 1 0.75 1.048k7 -1.85836 111.4	
Atom 2	1		0.85395 0.75 (Eq. (15.114))	0.81549			0.91140 (Eq. (15.116))				1 1			0.81549	0.91771 0.75	0.91771 0.75	0.91771 0.75	
on Aton I	0.86359		0.91771	0.81549			0.81549	0.86359			0.86359			0.81549	0.87495	0,87495	0.87495	
Crassessing Atom 2 Atom 2 Atom 2 Designation (Table 15.3.A)	н		-13.61806 0	-16.68411" 24 O ₈ 24			-14.53414 N	ж			н			-16,68412 25	-14,82575 I	-14,82575	-14.82575 I	
Atom 1 E. Hybridization Designation (Table 15.3.A)	7		-	24			7]- , 52	7	-		7			25	30	25	٠,	
$E_{\rm t'oulowhe}$ or $E$	-15.75493		-14.82575 C	יופיפאלון. רופיפאלון			-16,68412	-15.75493			-15,75493			-16.68412	-15 53033	-15.55033	-15.35033 C,	
2c' Terminal Alonas (a _n )	3.4252	_	3.7238	4.1231			4,472)	3.4252			3,4252			4.7958	4.1633	4.1633	4.7958	
2c' Bond 2 (a _n )	2.09711		2,71287	2.27630			2.65661	211106			2.09711			2.91547	2.11323	2,09711	2,90327	
2c' Bond 1 (a ₀ )	2.09711		2.09711	2.27630			2.71287	2,11106			2.09711			2.91547	2,91547	2 91547	2.90327	
Nemie of Nugls $2c^{1}$ $2c^{1}$ $2c^{2}$ Atomic of Lydic 18 $2c^{1}$ $2c^{2}$ $2c^{2}$ Atomic $2c^{2}$ Atomic $2c^{2}$ Atomic $2c^{2}$ Atomic $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ Atomic $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{2}$ $2c^{$	Matini ZHC_H	ο".)"H7	0"2"H7	,0N,02	°00"07	ZO,,NO.	<i>พื</i> ่0⊅7	Methylane .  ZHC", H	2,"3.	H',5",57	Hctivi ZHC."H	75.7.7	H".5".37	بعد ر" 7ر. د"ر"	".) "" H".)".)7	H, J, ', Y,	ימו (." "לנ"ל."	70,007

# CYCLIC AND CONJUGATED ALKENES

$$(C_n H_{2n+2-2m-2c}, n=3,4,5...\infty, m=1,2,3..., c=0 \text{ or } 1)$$

The cyclic and conjugated alkenes are represented by the general formula  $C_nH_{2n+2-2m-2c}$ ,  $n=3,4,5...\infty$ , m=1,2,3..., c=0 or 1 where m is the number of double bonds and c=0 for a straight-chain alkene and c=1 for a cyclic alkene. They have at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. Consider the cyclic and conjugated alkenes 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, five distinct C-C functional groups can be identified as given in Table 15.208. The designation of the structure of the groups are shown in Figures 61A-E. In addition,  $CH_2$  of any  $-C=CH_2$  moiety is an conjugated alkene functional group. The alkyl portion of the cyclic or conjugated alkene may comprise at least one terminal methyl group  $(CH_3)$ , and may comprise methylene  $(CH_2)$ , and methylyne 15 (CH) functional groups that are equivalent to those of branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the 2s and 2p AOs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. The C-C groups are solved in the same manner as those of the 20 branched-chain alkanes given in the corresponding section. For example, the cyclopentene  $C_a-C_b$  group is equivalent to the n-C-C alkane group. Many of the corresponding energies of the molecules of this class are similar, and they can be related to one another based on the structure. For example, cyclopentadiene is formed by ring closure of 1,3-pentadiene with the elimination of H from the terminal methyl and methylene groups. Thus, the energy of each of the corresponding carbon-carbon bonds in cyclopentadiene is the same as that in 1,3-pentadiene except that the difference between the energies of the 1,3-pentadiene  $C_c-C_d$  and the cyclopentadiene  $C_a-C_b$  groups is the magnetic energy (Eq. (15.58)) which is subtracted from the  $C_a-C_b$  total bond energy according to Eqs. (13.524-13.527) due to the formation of a CH group from the methylene group.

30  $E_r(atom-atom, msp^3.AO)$  of the C=C-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene,  $-2.26759 \ eV$ , given by

Eq. (14.247).  $E_T(atom-atom,msp^3.AO)$  of each C-C-bond MO in Eq. (15.52) is -2.26759~eV or -1.85836~eV based on the energy match between the  $C2sp^3$  HOs corresponding to the energy contributions equivalent to those of alkene, -1.13379~eV (Eq. (14.247)), or methylene, -0.92918~eV (Eq. (14.513)), groups, respectively, that are contiguous with the C-C-bond carbons. In the former case, the total energy of the C-C bond MO is matched to that of the alkane energy in the determination of the bond length. The charge density of 0.5e must be donated to the C-C bond in order to match the energy of the adjacent flanking double bonds. This further lowers the total energy of the C-C-bond MO and increases the C-C bond energy. This additional lowering of the C-C-bond energy by additional charge donation over that of an alkane bond due to adjacent double bonds is called *conjugation*.

The symbols of the functional groups of cyclic and conjugated alkenes are given in Table 15.207. The structures of 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene are shown in Figures 61A-E, respectively. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of cyclic and conjugated alkenes are given in Tables 15.208, 15.209, and 15.210, respectively. The total energy of each cyclic or conjugated alkenes given in Table 15.211 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.210 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of cyclic and conjugated alkenes determined using Eqs. (15.79-15.108) are given in Table 15.212.

Table 15.207. The symbols of functional groups of cyclic and conjugated alkenes.	ups of cyclic and conjugated alkenes.
Functional Group	Group Symbol
CC double bond	)=)
1,3-butadiene, 1,3-pentadiene C, -C;	83.5.3
1,3-cyclopentadiene (', -(',	( –( (4)
1,3-pentadiene (; -(',	V9 :3-:3
cyclopentene (', -(',	(6)
1,4-pentadiene (', -(',	(. (c)
1,3-cyclopentadiene (", -(',	(p))—)
cyclopentene (", -(",	(, – (, (¢)
CH; alkenyl group	$C - H\left(CH_2\right)$ (i)
CH, group	$C \rightarrow H \left(CH_3\right)$
CH ₂ aikyl group	$C - H\left(CH_2\right)$ (ii)
HO	r-H

Table 15.208. 7	Table 15.208. The geometrical bond parameters of cyclic and conju	neters of cyclic and conju	gated alkenes and experimental values [1]	mental values [1].			i	i	i	
Parameter	C=C Group	('-(' (a) Group	('-(' (b) Group	Oroup	C-(.(q) Group	ر، – ر. (e) Group	$C-H\left(CH_{2}\right)$ (i) Group	$C-H$ $(CH_3)$ Group	$C-H$ $(CH_2)$ (ii) Group	Group
$a(a_{\mathfrak{o}})$	1.47228	1.91256	2.04740	2,04740	2.04740	2.12499	1.64010	1,64920	1.67122	1.67465
c' (a ₀ )	1,26661	1.38295	1.43087	1,43087	1,43087	1,45773	1.04566	1.04856	1.05553	1.05661
Bond Length 2c' (A)	1.34052	1,46365	1.51437	1.51437	1.51437	1.54280	1.10668	1.10974	1.11713	1.11827
Exp. Bond Length (A)	1.349 (1,3-butadiene) 1.342 (1,3-cyclopentadiene) 1.342 (cyclopentene)	1.467 (1,3-butadiene) 1.469 (1,3-cyclopentadiene)	1.519 (eyclopentene)		1.509 (1,3-cyclopentadiene)	1.546 (cyclopentene)	1.10 (2-methylpropene) 1.108 (avg.) (1,3-butadiene)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)
b,c (a _a )	0.75055	1.32110	1.46439	1,46439	1.46439	1.54615	1.26354	1.27295	1.29569	1.29924
2	0.86030	0.72309	0.69887	0.69887	0.6987	0.68600	0.63756	0.63580	0.63159	0.63095

Table 15.209. The MO to HO intercept geometrical bond parameters of cyclic and conjugated alkenes	metrical bon	d parameters of o	yelic and conju	gated alkenes	$R_i$ is an alkyl group and $R_iR_i$ , $R^*$ are $H$ or alkyl groups. $E_i$ is $E_i(alom - alom, msp^3.AO)$	oup and R,R', I	?" are H or all	kyi groups. $E_{ m r}$	r is E_(atom-	-atom,msp³.AC	<u>~</u>				
Bond	Atom	E ₇ (eV) Bond (	E _T (eV) Bond 2	Ε̈́ _τ (eV) Bond 3	E _r (eV) Bond 4	Final Total Energy (7.2sp³ (eV)	research (an)	$(a_0)$	Erona (C2tp²) (eV) Final	$E(C2sp^3)$ (eV) Final	(e) . <i>θ</i>	(e)	(e) F	(a ₀ )	$\begin{pmatrix} a_2 \\ a_0 \end{pmatrix}$
$H_2C_a = C_b(H)(H)C = CR$ (1.3-batadiene, 1.3-pantadiene) $H_2C_a = C_b(H)C_b(H_2C_b(H)$ (1.4-pantadiene)	ئ د	-1.13380	g	<b>.</b>	-	-132.74949	17716-0	0.85252	-15,95955	-15.76868	129.84	50,16	60.70	0,72040	0.34620
$H_2C_a = C_A(H)(H)C = CR$ (1.3-buttadiene, 1.3-pontadiene) $-HC_3 = C_2(H)(H)C_2 = C_3H -$ (1.3-evelopentadiene)	ਹਾਂ ਹਾਂ -	-1.13380	-1,1338G	e	e	-153.88328	17718.0	79597	-17.09334	-16.90248	127.13	52.87	£7.73	0.78613	0.48047
$H_2C_a = C_1(H)(H)C_A = C_2(H)C_2H_3$ (1.3-pentadione) $H_2C_a = C_4(H)(C_4G_2(H) = C_4H_2$ (1.4-pentadione) $-HC_3 = C_2(H)(H)C_2 = C_4H - C_4G_2$ (1.3-cyclopentadione) (1.3-cyclopentadione) (1.3-cyclopentadione)	ಆಆಆ	-1.13380	41,020,04	÷	-	-153,67867	17716 0	0.80361	-16.88873	-16.69786	127.61	52.39	58.24	0.77492	0,49168
$K' = C_{b,a}(H) - (H)C_{b,a} = CR'$ $(C - C'(a))$	ر ال	-1.133%	-1.13380	0	0	-153,88328	0.91771	0.79597	-17.09334	-16.90248	78.31	101.69	36.16	1.54418	0,16123
$H_{\mathcal{L}'_s} = C_{s,t}(H)(H)C_s = C_s(H) - C_sH_s$ $(1,3\text{-pentadiene})$ $-H_{\mathcal{L}'_s} - C_s(H) = (H)C_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_sH_s - C_s$	ಲ್ ಆ	-1,13380	-0.9291X	5	0	-153.67867	0.91771	0,80561	-16.88873	-16.69786	64.57	£F.511	Ø.83	1.77684	0.34596
$H_{\mathfrak{g}}C_{\mu} = C_{\mathfrak{g}}(H)(H)(C_{\mu} = C_{\mathfrak{g}}(H) - C_{\mu}H_{\mathfrak{g}}$ (1,3-pentadiene) (C - C'(b))	ڻ	-0,92918	Û	0	0	-152.54487	0.91771	0,86359	-15.75493	-15.36407	72.77	107.73	34.17	1.69348	0,26301
$-H_2C_k - C_k(H) = (H)C_k - C_kH_2 - (cyclopentene)$ (cyclopentene) (C - C_(b))	ڻ	-0.92918	81626'0-	0	0	-153,47405	0.91771	0.81549	-16.68411	-16.49325	62.39	[[4,0]	30.58	1.76270	0.33183
$H_2C_x = C_x(H) - C_x H_2C_y(H) = C_x H_2$ (1.4-pentatione) (1.4-c) (1.4-c) $-H_2C_x - HC_x = C_x(H)(H)C_x = C_x H - C_x H$ (1.3-cyclopentadiene) (1.3-cyclopentadiene)	e e	-1,13380	-0.92918	5	6	-153.67866	0.91771	0,80561	-16.88873	-16.69786	64.57	115.43	29.79	1.77684	0.34596
$H_2C_x = C_x(H) - C_xH_2C_x(H) = C_xH_2$ (1,4-pentadiene) (C,-C; (e)) $-H_2C_x - HC_x = C_x(H)(H)C_x = C_xH -$ (C,-C; (d)) (C,-C; (d))	లి లో	-0.92918	81626'0-	Đ	O	-153,47405	0.91771	0.81549	-16.68411	-16,49325	66.59	11,01	30.58	1.76270	0.33183
$-H_2C_u - H_2C_4C_4(H) = (H)C_2C_2H_2 - (\operatorname{cyclopentene})$ (cyclopentene) (C - C (e))	נ'ינ'	-0.9291K	N1676'0-	8	0	-153,47405	12216.0	0.81549	-16,68411	-16,49325	56.41	(23.59	26.06	1.90890	0.45116
$C-H\left(CH_{3}\right)$ (i)	C	-1.13380	0	O	0	-152.74949	17716.0	0.85252	-15.95955	-15,76868	77.15	102.85	41.13	1,23531	0.18965
C-H (CH ₃ )	υ	41,92918	0	ß	n	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41,48	1,23564	0.18708
$C-H$ $(CH_1)$ (ii)	i.	-0.92918	-0.92918	0	0	-153.47406	17716.0	0,81549	-16,68412	-16,49325	68.47	111.53	35.84	1.35486	0.29933
C-H (CH)	ن	-0,92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.77247	-17,61330	-17.422#	61.10	118.90	31.37	1.42988	0,37326

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Table 15.210. The energy parameters (eV) of functional groups of cyclic and conjugated alkenes.	rs (eV) of function	nal groups of cycin	and conjugated a	келеѕ.						
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Parameters	C=C	(. – (. (a)	ر ِ – ر. (p)	(; – (; (e)	(p)	(a) ) ~ (b)	CH ₂ (i)	$CH_3$	$CH_{2}$ (ii)	<i>H−</i> 2
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		Group	Group	Group	dnorio	Group	Croup	Group	Group	Group	Group
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	n'	61	_	_		1	1	2	3	2	1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	11,	0	0	0	0	0	0	1	2	1	0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	n,	0	0	0	0	0	0	0	0	0	0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C,	0.5	5,0	0.5	0.5	0.5	0.5	0.75	0.75	0.75	51.0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	·:	0,91771	_	-	_	-	_	1	1	I	1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5	-	_	-	-	-	-	-	1	1	1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	6,	17716.0	0.91771	0,91771	0.91771	17716.0	0.91771	17710	0.91771	0.91771	0.91771
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5	0	O	0	0	-	0	1	0	1	1
•         0         0         0         0         0         2           •         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.5         0.7         0.7         0.7         0.7         0.7         0.7         0.7         0.7         0.7         0.7         0.7         0.7         0.7         0.7         0.7         0.7	5	4	2	2	2	2	2	1	1	1	1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		0	0	0	0	0	0	2	3	2	1
1	ر ا	0.5	5,0	0.5	6.5	5.0	5.0	0.75	0.75	52.0	0.75
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	ڙ.:	0.91771	1	1	1	-	-	1	1	1	1
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	V, (eV)	-102.08992	-33.01226	-30.19634	-30.19634	-30.19634	-28.79214	-72.03287	-107.32728	-70.41425	-35.12015
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	V, (eV)	21.48386	9.83824	9.50874	9.50874	9,50874	9.33352	26.02344	38.92728	25.78002	12.87680
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	T' (eV)	34.67062	8.63041	7.37432	7.37432	7,37432	6.77464	21,95990	32.53914	21.06675	10.48582
eV )         0 · · · · · · · · · · · · · · · · · · ·	V, (eV)	-17.33531	-4.31520	-3.68716	-3.68716	-3.68716	-3.38732	-10.97995	-16.26957	-10.53337	-5.24291
Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part   Part	E(40 10) (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-14.63489	-15,56407	-15.56407	-14.63489
(eV)         0         -12,77653         -14,63489         -14,63489         -15,63607         -14,63489           eV)         -63,27075         -31,63534         -31,63534         -31,63534         -31,63537         -49,66437           -alm,mxp³,AO) (eV)         -2,26759         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,88836         -1,866437         -1,666437         -1,666437         -1,666437         -1,666437         -1,666437         -1,666437         -1,666437         -1,666437         -1,66643         -1,66437         -1,66437         -1,66437         -1,66437         -1,66437         -1,66437         -1,66437         -1,66437         -1,66437         -1,66437         -1,66437         -1,66437         -1,66437         -1,66439         -1,66439         -1,66439         -1,166439         -1,116643         -1,116643	$\Delta E_{H,MO}$ (no no) (eV)	0	-1.85836	0	0	0	0	0	0	0	0
eV)         -63.27075         -31.63534         -31.63534         -31.63537         -49.66437 $eV$ )         -c65.3833         -2.26759         -1.85836         -1.85836         -1.85836         -1.85836         -1.85836         -1.85836         -1.85836         -1.85836         -1.85836         -1.85836         -1.85836         -1.85836         -1.85836         -1.85836         -1.85836         -1.85836         -1.85836         0 $A$ )         -65.53833         -33.90295         -33.49373         -33.49373         -33.49373         -49.66493         0 $A$ ) $A$ 3.0680         11.0522         9.97851         23.3391         9.97851         9.43699         25.2077 $A$ $A$ 3.0680         11.0522         9.97851         23.3391         9.97851         9.43699         25.2077 $A$ $A$ 3.0680 $A$ 3.0690         -0.16982         -0.15982         -0.16982         -0.16982         -0.16982         -0.16982         -0.16982         -0.16982         -0.16982         -0.11402         0.11420         0.11420         0.11420         0.11420         0.11420         0.11420         0.11420         0.11420         0.11420         0.11420         0.11420         0.11420         <	$E_T(x_1 m) (eV)$	0	-12.77653	-14.63489	-14.63489	-14.63489	-15.56407	-14.63489	-15.56407	-15.56407	-14.63489
Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colombo   Colo	$\mathcal{E}_{T}(n_{1}\omega)$ (eV)	-63.27075	-31.63535	-31.63534	-31.63534	-31.63534	-31.63537	-49.66437	-67.69451	-49.66493	-31.63533
J/S         -65.53833         -33.40295         -33.40373         -33.49373         -33.49373         -49.66493           dI/s         43.0680         11.0522         9.97851         23.3291         9.97851         9.43699         25.2077           d         28.34813         7.27475         6.56803         15.3563         6.56803         6.21159         16.59214           -0.34517         -0.18090         -0.16982         -0.25966         -0.16982         -0.16982         -0.16515         -0.25493           f ld         [48]         [12]         [12]         [12]         [13]         6.1159         0.11348           e         -0.25568         -0.10676         -0.11402         -0.20386         -0.11402         -0.10359         -0.07727           e         -0.25568         -0.10676         -0.11402         -0.20386         -0.11402         -0.10359         -0.07727           e         -0.4803         0.14803         0.14803         0.14803         0.14803         0.14803         0.14803         0.14803         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.634	$E_T(atom - atom, msp^3.AO)$ (eV)	-2,26759	-2.26759	-1.85836	-1.85836	-1.85836	-1.85836	0	0	0	0
d1s)         43.0680         11.0522         9.97851         23.3291         9.97851         9.43699         25.2077           28.34813         7.27475         6.56803         15.3563         6.56803         6.21159         16.5214           0.34517         0.18090         0.16982         0.25966         -0.16515         -0.2493           0.17897         0.14829         0.11159         0.11159         0.11319         0.12312         0.35532           161         1481         1[2]         1[2]         1[2]         1[2]         Eq. (13.458)           0.25568         -0.10676         -0.11402         -0.20386         -0.10402         -0.10359         -0.10359           17)         -66.04969         -34.00972         -33.69776         -33.69776         -33.59732         -49.81948           10] eV)         0         0         0         0         0         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63489         -14.63	$E_T(so)$ (eV)	-65,53833	-33.90295	-33.49373	-33.49373	-33,49373	-33,49373	-49,66493	-67.69450	-49,66493	-31.63537
28.34813   7.27475   6.56803   15.35563   6.51893   6.21159   16.59214     -0.34517   -0.18090   -0.16982   -0.25966   -0.16982   -0.16515   -0.25493     -0.17897   0.14829   0.11159   0.11159   0.12312   0.35532     -0.25568   -0.10676   -0.11402   -0.10402   -0.10359   -0.07727     -0.25568   -0.10676   -0.11402   -0.10403   0.14803   0.14803     -0.14803   0.14803   0.14803   0.14803   0.14803   0.14803     -0.16569   -0.10676   -0.11402   -0.10359   -0.07727     -0.16369   -0.1463489   -0.1463489   -0.1463489   -0.1463489   -0.1463489     -0.16369   -0.1463489   -0.1463489   -0.1463489   -0.1463489   -0.1463489     -0.16369   -0.16369   -0.1463489   -0.1463489   -0.1463489     -0.16369   -0.1463489   -0.1463489   -0.1463489   -0.1463489     -0.16369   -0.16676   -0.1463489   -0.1463489   -0.1463489     -0.16369   -0.16676   -0.1463489   -0.1463489   -0.1463489     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.1463489   -0.1463489   -0.1463489   -0.1463489     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.16369   -0.16676   -0.16676   -0.16676   -0.16676     -0.1	$\omega \left(10^{15} rud/s\right)$	43.0680	11.0522	9.97851	23,3291	9.97851	9.43699	25.2077	24.9286	24.2751	24.1759
-0.24517   -0.18090   -0.16982   -0.15966   -0.16982   -0.16515   -0.25493   -0.17897   0.14829   0.11159   0.11159   0.11159   0.12312   0.35532   -0.25568   -0.10676   -0.11402   -0.20386   -0.11402   -0.10559   -0.07727   -0.25568   -0.10676   -0.11402   -0.10359   -0.10359   -0.07727   -0.14803   0.14803   0.14803   0.14803   0.14803   0.14803   0.14803   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -14.63489   -1	$E_K$ (eV)	28,34813	7.27475	6.56803	15.35563	6.56803	6,21159	16,59214	16.40846	15.97831	15.91299
0.17897   0.14829   0.11159   0.11159   0.11159   0.12312   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.35532   0.355322   0.355322   0.355322   0.355322   0.355322   0.3555322   0.355522   0.355522   0.355522   0.35552   0.35552   0.35552   0.35	$\vec{E}_{n}$ (eV)	-0.34517	-0.18090	-0.16982	-0.25966	-0.16982	-0.16515	-0.25493	-0.25352	-0.25017	-0.24966
Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colorer   Colo	$\vec{E}_{\Lambda r b}$ (eV)	0.17897	0.14829	0.11159	0.11159	0.11159 [12]	0.12312	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)
(V)         -66,04969         -34,00972         -33,60776         -33,69760         -33,60776         -33,60776         -33,60776         -33,69760         -33,60776         -33,59732         -49,81948           (w)         (eV)         -14,63489         -14,63489         -14,63489         -14,63489         -14,63489           (v)         0         0         0         0         -13,59844           (v)         7,51014         4,71994         4,37782         4,18995         4,37754         7,83968	$\vec{E}_{nc}$ (eV)	-0.25568	-0.10676	-0.11402	-0.20386	-0.11402	-0.10359	-0.07727	-0.22757	-0.14502	-0.07200
-66,04969         -34,00972         -33,60776         -33,60776         -33,60776         -33,60776         -33,59732         -49,81948           1         -14,63489         -14,63489         -14,63489         -14,63489         -14,63489         -14,63489         -14,63489         -13,59844           0         0         0         0         0         -13,59844           7 5,1014         4 71994         4 37798         4 47782         4 18995         4 37754         7 83368	$E_{m_{\rm K}}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
14,63489	$E_{T}(\mathrm{tirup})$ (eV)	-66.04969	-34.00972	-33.60776	-33.69760	-33.60776	-33.59732	-49.81948	-67.92207	-49.80996	-31.70737
0         0         0         0         0         -13,59844           7 5 10 14         4 77994         4 37798         4 47782         4 18995         4 37754         7 83968	E untal (c1. 10 110) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489
7 21995 4 32754 7.83968	$E_{unn,d}(\epsilon_s \text{ so no}) (eV)$	0	0	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844
	$E_{D}(c_{may})$ (eV)	7.51014	4.73994	4,33798	4.42782	4.18995	4.32754	7.83968	12.49186	7.83016	3.32601

Table 15.211. The total bond energies of cyclic and conjugated alkenes calculated using the functional group composition and the energies of Table 15.210 compared to the experimental values [2]. The magnetic energy E_x that is subtracted from the 5 weighted sum of the  $E_{n}_{\text{(timp)}}$  (eV) values based on composition is given by (15.38).

J Weigure	weighted sum of the Entrant (er ) van	ß	נפריכו) לפ וואינק מי ווטווומטקוווטט ווט בססמט	HOMES STREET	7 (10.00).										
Formula	Name	ر=ر ر=ر	ı	('-('(a) ('-('(b) ('-('(c)	(2) (3)	(p) ()-()	C-C (d) C-C (e)	CH (I)	CH	CH. (II)	СН	12	Calculated	Experimental	Relative
		)								··· 2 (···)		Som J	Total Bond	Total Bond Energy	Error
											i		Energy (eV)	(eV)	
C.H.	1,3 Butadiene	2	-	0	0	0	0	7	0	0	2	0	42,09159	42,12705 0	0.00084
H. U	1,3 Pentadiene	7	-	-	0	0	0	-	_	0	0	0	54,40776	54,42484	0,00031
, th	1.4 Pentadiene	cı	0	0	7	0	0	C1	0	_	7	0	54.03745	54,11806	0.00149
CH	1.3 Cyclopentadiene	C1	_	0	0	2	0	0	0		4	0	49.27432	49,30294	0.00058
H.O	Cyclopentene		0	7	0	0	7	0	0	m	7	~	54.83565	54,86117	0,00047
	l														

						<del></del>				
Exp. $\theta$ (°)		120.9 (1,3-butadiene)	120.9 (1,3-butadiene)	(13-burneline CC) (13-burneline CC) (13,5-braziline Cb.CC) (13,5-braziline Cb.CC) (13,5-braziline CeCbC) (13,5-braziline CeCbC) (2,5-braziline CeCbC) (2,5-braziline CeCbC)	109.4 (1,3-cyclopentadiene)	109.3 (1,3-cyclopentadiene)	102.8 (1,3-cyclopentadiene)	110.0 (cyclopentene)	103.0 (cyclopentene)	104.0 (cyclopentene)
Cal. <i>9</i>	113.25	123.38	119.45	124.48	108.44	108.47	102.41	110.14	102.85	103.61
(°)										
( _o )		113.25								
φ ( ₀ )										
$E_T$	0		0	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836
70"	1.17300		1.00000	0.85395	0.76360	0.77247	0.78155	D.77701	0.78620	0.79085
· c	0.75		0.75	<u>.</u>	_ **		_		-	- 
J.	-		-	-		-	<b>-</b> .	_	-	-
υ	_		0.75	-	1	-	_		-	_
C ₂ Atom 2			0.85252	0.79597	0,76360	0,77247	0.78155	0.77247	0,78155	0.79085
C ₂	0.85252		0.85252	0.80561	0.76360	0.77247	0.78155	0,78155	0.79085	0.79085
Atom 2 Hybridization Designation (Table 15.3.A)	н		6	. 30	46	42	38	42	38	35
E Custombre Atom 2	н		-15.95954 C _h	-17,09334 (',	-17.81791	-17.61330 C.	-17.40869	-17.61330 C,	-17.40869 ('.	-17.20408 C,
Atom I Hybridization Designation (Table 15.3.A)	6	İ	6	7.7	46	42	38	38	35	35
E'entoube Alon I	-15.95955		-15.95954	.16.88873	-17.81791	-17,61330 (°,	-17.40869	-17.40869 C,	-17.20408	-17.20408 (',
2c' Terninal Atens (u0)	3.4928		4.0000	4,6904	4.3012	4.3818	4,4609	4.4272	4.5166	4,5826
2c' Band 2 (u0)	2.09132		2.09132	2.76590	2.76590	2.53321	2.86175	2,53321	2.86175	2.91548
2c' Band 1 (a ₀ )	2.09132		2,53321	2.53321	2.53321	2.86175	2.86175	2.86175	2,91548	2.91548
Atoms of Anglio	$\angle HC_nH$ $H_2C_n = C_n$ 1,3-butadiene	$\angle C, C, H_a$ $H_2C_a = C_b$ 1,3-butadiene	$\angle C_i C_i H_i$ $H_i C_i = C_i$ 1,3-butadiene	کر"ک" ر" = د", د" 1,3-butadiene	$\angle C_r C_r C_r$ $C_s = C_r C_r$ 1,3-cyclopentadiene	$ZC_{\nu}C_{\nu}C_{\nu}$ $C_{\nu}C_{\nu}=C_{\nu}$ 1,3-cyclopentadiene	$\angle C_{r}C_{r}C_{r}$ $= C_{r}HC_{r}H_{z}C_{r}(H) = 1.3-\text{eyelopentadiene}$	$\angle C_{k}C_{k}C_{k}$ $-H_{2}C_{k}HC_{k}=C_{k}HC_{k}H_{2}-C_{k}HC_{k}H_{2}$	$\angle C'_{i}C_{i}C_{i}$ $-H_{2}C_{i}H_{2}C_{i}H_{2}C_{i}H_{2}$ exclopentene	$\angle C_r C_r C_r$ $-C_r H_2 C_r H_2 C_r H_2$ exclonentene

## AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple  $H_2$ -type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule  $(C_6H_6)$  section can be generalized to any aromatic function group(s) of aromatic and heterocyclic compounds.

 $C_6H_6$  can be considered a linear combination of three ethylene molecules wherein a C-H bond of each  $CH_2$  group of  $H_2C=CH_2$  is replaced by a C=C bond to form a six-10 member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule  $(CH_2CH_2)$  section. The radius  $r_{ethylene2sp^3}$  (0.85252 $a_0$ ) of the  $C2sp^3$  shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy  $E_{Coulomb}(C_{ethylene}, 2sp^3)$  (-15.95955 eV) of the outer electron of the  $C2sp^3$  shell is given by Eq. (14.245). The energy  $E(C_{ethylene}, 2sp^3)$  (-15.76868 eV) of the outer electron of the  $C2sp^3$  shell 15 is given by Eq. (14.246).  $E_T(C=C,2sp^3)$  (-1.13380 eV) (Eq. (14.247), the energy change of each  $C2sp^3$  shell with the formation of the C=C-bond MO is given by the difference between  $E(C_{ethylene}, 2sp^3)$  and  $E(C, 2sp^3)$ .  $C_6H_6$  can be solved using the same principles as those used to solve ethylene wherein the 2s and 2p shells of each C hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two C2sp3 hybridized orbitals 20 (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each 2sp3 HO of each carbon atom initially has four unpaired electrons. Thus, the 6 H atomic orbitals (AOs) of benzene contribute six electrons and the six  $sp^3$ -hybridized carbon atoms contribute twenty-four electrons to form six C-H bonds and six C = C bonds. Each C - H bond has two paired electrons with one donated from the H AO 25 and the other from the  $C2sp^3$  HO. Each C=C bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two C2sp3 HOs of the participating carbon atoms. Each C-H and each C=C bond comprises a linear combination of one and two diatomic  $H_2$ -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

Consider the case where three sets of C = C-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds 5 comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the  $C2sp^3$  HOs:

$$\begin{pmatrix}
3(2 C2sp^3 + 0.75 H_2 MO) \rightarrow 3(C=C) - ethylene - type - bond MO \\
\rightarrow 6(C=C) - bond MO of benzene
\end{pmatrix} (15.142)$$

10 The linear combination of each  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution per bond from each  $C2sp^3$  HO to the C=C-bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond C=C-bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the C=C-bond MO of ethylene (Eqs. (14.242-15.14.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each C=C-bond gives rise to the  $C_{benzene}2sp^3$  HO-shell Coulombic energy  $E_{Coulomb}\left(C_{benzene},2sp^3\right)$  given by Eq. (14.245). To meet the equipotential condition of the union of the six  $C2sp^3$  HOs,  $c_2$  and  $c_3$  of Eq. (15.42) for the aromatic C=C-bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of  $E_{Coulomb}\left(C_{benzene},2sp^3\right)$  (Eq. (14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $E_{Coulomb}\left(C_{benzene},2sp^3\right)$  (Eq. (14.245)).

$$C_2(benzeneC2sp^3HO) = c_2(benzeneC2sp^3HO) = \frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252$$
 (15.143)

The energies of each C=C bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of benzene. Ethylene serves as a basis element for the C=C bonding of benzene wherein each of the six C=C bonds of benzene comprises (0.75)(4)=3 electrons according to Eq. (15.142).

The total energy of the bonds of the eighteen electrons of the C = C bonds of benzene,  $E_T \left( C_6 H_6, C = C \right)$ , is given by (6)(0.75) times  $E_{T+osc}(C = C)$  (Eq. (14.492)), the total energy of the C = C-bond MO of benzene including the Doppler term, minus eighteen times  $E(C, 2sp^3)$  (Eq. (14.146)), the initial energy of each  $C2sp^3$  HO of each C that forms the C = C bonds of bond order two. Thus, the total energy of the six C = C bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$E_{T}\left(C_{6}H_{6}, C=C\right) = (6)(0.75)E_{T+osc}\left(C=C\right) - (6)(3)E\left(C, 2sp^{3}\right)$$

$$= (6)(0.75)\left(-66.05796 \ eV\right) - 18\left(-14.63489 \ eV\right)$$

$$= -297.26081 \ eV - \left(-263.42798 \ eV\right)$$

$$= -33.83284 \ eV$$
(15.144)

The results of benzene can be generalized to the class of aromatic and heterocyclic compounds.  $E_{h\nu}$  of an aromatic bond is given by  $E_T (H_2)$  (Eqs. (11.212) and (14.486)), the maximum total energy of each  $H_2$ -type MO such that

$$\overline{E}_{osc} = n_{\rm l} \left( \overline{E}_D + \overline{E}_{Kvib} \right) = n_{\rm l} \left( -31.63536831 \ eV \sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$
 (15.145)

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two given in the Benzene Molecule  $(C_6H_6)$  section modifies Eqs. (15.52-15.56). Multiplication of the total energy given by Eq. (15.55) by  $f_1 = 0.75$  with the substitution of Eq. (15.145) gives the total energy of the aromatic bond:

$$E_{T}(Group) = f_{1} \left( E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO) - 31.63536831\ eV \sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}} - \frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}}{m_{e}} + n_{1}\overline{E}_{Kvih} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}}} \right)$$
(15.146)

The total bond energy of the aromatic group  $E_D(Group)$  is the negative difference of the total energy of the group (Eq. (15.146)) and the total energy of the starting species given by the sum of  $c_4 E_{initial}(c_4 AO/HO)$  and  $c_5 E_{initial}(c_5 AO/HO)$ :

$$E_{D}(Group) = - \begin{pmatrix} f_{1} \\ -31.63536831 \text{ eV} \\ -\left(c_{4}E_{initial}(AO/HO) + c_{5}E_{initial}(c_{5}AO/HO)\right) \end{pmatrix}$$
(15.147)

5 Since there are three electrons per aromatic bond,  $c_4$  is three times the number of aromatic bonds.

Benzene can also be considered as comprising chemical bonds between six CH radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of CH is given in the Hydrogen Carbide (CH) section. Those of the benzene are given in the Benzene Molecule  $(C_6H_6)$  section. The energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  are the same as those of the hydrogen carbide radical, except that  $E_T(C=C,2sp^3)=-1.13379~eV$  (Eq. (14.247)) is subtracted from  $E_T(CH)$  of Eq. (13.495) to match the energy of each C-H-bond MO to the decrease in the energy of the corresponding  $C2sp^3$  HO. In the corresponding generalization of the aromatic CH group, the geometrical parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with  $E_T(atom-atom, msp^3.AO)=-1.13379~eV$ .

The total energy of the benzene C-H-bond MO,  $E_{T_{benzene}}\left(C-H\right)$ , given by Eq. (14.467) is the sum of  $0.5E_{T}\left(C=C,2sp^{3}\right)$ , the energy change of each  $C2sp^{3}$  shell per single bond due to the decrease in radius with the formation of the corresponding C=C-bond MO (Eq. (14.247)), 20 and  $E_{T_{benzene}}\left(CH\right)$ , the  $\sigma$  MO contribution given by Eq. (14.441). In the corresponding generalization of the aromatic CH group, the energy parameters are determined using Eqs. (15.146-15.147) with  $f_{1}=1$  and  $E_{T}\left(atom-atom,msp^{3}.AO\right)=\frac{-1.13379\ eV}{2}$ . Thus, the energy

contribution to the single aromatic CH bond is one half that of the C=C double bond contribution. This matches the energies of the CH and C=C aromatic groups, conserves the electron number with the equivalent charge density as that of s=1 in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic C=C bonds to give CH groups creates unpaired electrons in these fragments that corresponds to  $c_3=1$  in Eq. (15.56) with  $E_{max}$  given by Eq. (15.58).

Each of the C-H bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each C-H bond,  $-E_{D_{benzene}}(^{12}CH)$  (Eq. (14.477)), the total energy of the twelve electrons of the six C-H bonds of benzene,  $E_T(C_6H_6, C-H)$ , given by Eq. (14.494) 10 is

$$E_T(C_6H_6, C - H) = (6)(-E_{D_{burgers}}(^{12}CH)) = 6(-3.90454 \ eV) = -23.42724 \ eV \tag{15.148}$$

The total bond dissociation energy of benzene,  $E_D(C_6H_6)$ , given by Eq. (14.495) is the negative

sum of 
$$E_T \left( C_6 H_6, C = C \right)$$
 (Eq. (14.493)) and  $E_T \left( C_6 H_6, C - H \right)$  (Eq. (14.494)):

$$E_{D}(C_{6}H_{6}) = -\left(E_{T}\left(C_{6}H_{6}, C = C\right) + E_{T}\left(C_{6}H_{6}, C - H\right)\right)$$

$$= -\left(\left(-33.83284 \ eV\right) + \left(-23.42724 \ eV\right)\right)$$

$$= 57.2601 \ eV$$
(15.149)

Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule ( $C_6H_6$ ) section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and hertocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 20 energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aromatics and hertocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each  $E_D$  (Group) of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.79-15.108) are given in Table 15.218.

and the second of the second

 Table 15.214. The geometrical bond parameters of aromatics and hertocyclics and experimental values [1].

 Parameter
 C = C CH Croup Croup
 C/H

 a (a, b)
 1.47348
 1.60061

 c' (a, b)
 1.31468
 1.03299

 Bond Length
 (1.3940
 1.101

 Exp. Bond Length
 (1.399)
 1.101

 A)
 (benzene)
 (benzene)

 h, c (a, b)
 0.66540
 1.22265

 e
 0.88223
 0.64537

5 Table 15.215. The MO to HO intercept geometrical bond parameters of benzene.  $E_T$  is  $E_T(atom - atom, msp^3.AO)$ .

Bond

For Example 15.215.

	$\begin{pmatrix} d_1 \\ (a_0) \end{pmatrix}$		0.21379		0.55533	20000
	(a ₀ )		1.24678		0.75935	2000
	θ ₂ (°)		38.84		58.98	
	θ' (•)		105.58		45,76	
	θ, ( _o )		74.42		134.24	
	$\tilde{E}(C2xp^3)$ (eV) Final		-16.90248		-16,90248	
	Econom (C25p²) (eV) Final		-17.09334		-17.09334	
	$(a_0)$		0.79597		0.79597	
	$(a_0)$		0.91771		0.91771	
	Final Total Energy (72.sp³		-153.88327		-153,88327	
	$E_r$ (eV) Bond 4		o		5	
	E _r (eV) Bond 3	0 27700	-0.30090	00000	060000	
-	E ₇ (eV) Bond 2	0.05035	CCOCO D-	0.05076	0.0.033	
-	(eV) Bond 1	-0 85035	eraen'a	-0.85025	-0.42.03	
Afons	Aloin	:	,	:	ja j	
Bond		(C-H(CH))	1	J- JH = J	, ,,,,,	

Table 15.216. The energy parameters (eV) of functional groups of aromatics and hertocyclics.

C=C	<i>CH</i> Group
0.75	1
2	. 1
0	0
0	0
0.5	0.75
0.85252	1
1	1
0.85252	0.91771
0	1
3	1
0	1
0.5	0.75
0.85252	1
-101.12679	-37.10024
20.69825	13.17125
34.31559	11.58941
-17.15779	-5.79470
0	-14.63489
0	-1.13379
0	-13.50110
-63.27075	-31.63539
-2.26759	-0.56690
-65.53833	-32.20226
49.7272	26.4826
32.73133	17.43132
-0.35806	-0.26130
0.19649 [49]	0.35532 Eq. (13.458)
-0.25982	-0.08364
0.14803	0.14803
-49.54347	-32.28590
-14.63489	-14.63489
0	-13.59844
5.63881	3.90454
	Group 0.75 2 0 0 0.5 0.85252 1 0.85252 0 3 0 0.5 0.85252 0 0.85252 -101.12679 20.69825 34.31559 -17.15779 0 0 0 -63.27075 -2.26759 -65.53833 49.7272 32.73133 -0.35806 0.19649 [49] -0.25982 0.14803 -49.54347 -14.63489 0

Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the experimental values [2].

			$\theta$ Exp. $\theta$	2 021 071	c-oclosi 61	
			Cal. <i>θ</i>	+	120.19	
			(°)	1		L
			θ (O)			
			φ (⊙)			
			$E_T$ (eV)		-1.85836	
			20"		0.79232	
Ì			J.		-	
			5	-	-	
			<u>ن</u>	-	-	
			C ₂	0.70737	707770	
			C ₂	0.79732		
Relative Error	0.00006	om, $msp^3.AO$ ).	Atom 2 Hybridization Designation	34		
Experimental Total Bond Energy (eV)	57.26340	is $E_{\tau}(atom-ah)$	Etadoning Ann 2	-17.17218		
Calculated Total Bond Tenergy (eV)		values [1]. E ₇	Atom   Hybridization Designation (Table [5.3.4)	34		
		sperimental	Econtropic Alon I	-17.17218		
CH	9	ne and e)	2c' Terninal Atoms (a,)	4.5585		
C = C	9	rs of benze	2c* Bond 2 (a,)	2.62936 2.62936 4.5585 -17.17218		
		e paramete	2c' Bond I (a _e )	2,62936		
Name	Benzene	Table 15.218. The bond angle parameters of benzene and experimental values [1]. $E_T$ is $E_T$ (atom – atom, msp ³ .AO).	Atons of Angle	ZC'C'C' (aromatic)	H.J.)7	romatic)
Formula	C,H	Table 15.2	₹	<u>.</u>		(a

## **NAPHTHALENE**

Naphthalene has the formula  $C_{10}H_8$  and comprises a planar molecule with two aromatic rings that share a common C-C group. In order to be aromatic, the total number of bonding electrons must be a multiple of 3 since the number of electrons of the aromatic bond is (0.75)(4)=3 as shown in the Benzene section. In the case of naphthalene, the peripheral 10 carbons form the aromatic MO with the center bridged by a C-C single bond. Then, 30 electrons of the 48 available form aromatic bonds, two electrons form the bridging C-C single bond, and 16 electrons form the eight C-H single bonds. The energies of the aromatic carbons are given by the same equations as those of benzene (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)), except that there are 10 in naphthalene versus six in benzene. Since there are three electrons per aromatic bond,  $c_4$  is three times ten, the number of aromatic bonds. Similarly, the aromatic C-H group of naphthalene is equivalent to that of benzene.

To meet the equipotential condition of the union of the ten  $C2sp^3$  HOs bridged by the C-C single bond, the parameters  $c_1$ ,  $C_2$ , and  $C_{2o}$  of Eq. (15.42) are one for the C-C group, 15  $C_{1o}$  and  $C_1$  are 0.5, and  $c_2$  given by Eq. (15.142) is  $c_2(C2sp^3HO) = 0.85252$ . Otherwise, the solutions of the C-C bond parameters are equivalent to those of the replaced C-H groups with  $E(AO/HO) = -14.63489 \ eV$  and  $\Delta E_{H_2MO}(AO/HO) = -1.13379 \ eV$  in Eq. (15.41). Similarly, the energy parameters are determined using Eqs. (15.52-15.56) with  $E_T(atom-atom, msp^3.AO) = \frac{-1.13379 \ eV}{2}$ .

The symbols of the functional groups of naphthalene are given in Table 15.219. The corresponding designation of the structure is shown in Figure 62. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of naphthalene are given in Tables 15.220, 15.221, and 15.222, respectively. The total energy of naphthalene given in Table 15.223 was calculated as the sum over the integer multiple of each  $E_D(c_{Polip})$  of Table 15.222 corresponding to functional-group composition of the molecule. The bond angle parameters of naphthalene determined using Eqs. (15.79-15.108) are given in Table 15.224.

	5								· ·	
!	Group Symbol	)-j	Trate 15 220. The peometrical bond parameters of naphitialene and experimental values [1].	droup Group	1.75607	1.32517	1.40250	1,42 (naphthalene)	1.15226	0.75462
	groups of naphing		trameters of naplith	CH Group	1,60061	1,03299	1.09327	1,101 (benzene)	1,22265	26363.0
	19. The symbols of functions Functional Group natic bond)	(puc	eometrical bond pa	C = C	1,47348	1.31468	1.39140	1.40 (avg.) (naphthalene)	0.66540	
	Table 15.219. The symbols of functional groups of naturnature.  Functional Group  C.C. (aromatic bond)	CH (aromatic) C, -C, (bridging bond)	Toble 15 220. The B	Parameter	2(a)	c' (a ₀ )	Bond Length	Exp. Bond Length	1000	(00) 250
										•

	(aº)		0.21379	0.55533	0.57038	0,14248		
a .	(g)		1,24678	0,75935	0.74430	1,18269		
92	©		38.84	58.98	39.66	47.66		
90"	<u> </u>		105.58	45.76	45.19	5	2000	
ιθ	©	;	74.42	134.24	13483	4	99.30	
(C) cn 3	(eV)	Final	-16,90248	-16.90248	2017 77	-10.61903	-16,61903	
(c., (m)	(eV)	Final	-17,09334	-17 09334		-16.80989	-16.80989	
	fead		0.79597	Politico C	0.1937	0.80939	0.80939	
	P. Careful	(a ₀ )	) or other	1//1610	0,91771	0.91771	122160	-
	-	Casp	(eV)	-153,88327	-153.88327	153,59983	-153 59983	
10m,msp'.AO}	E	(eV) Rond 4		٥	a	0		>
E, is E, (atom - atom, msp". AO).	E,	(eV)	c pilos	-0.56690	0.56690	-0.28345		-0,28345
anhthalene, E.	E.	(e ^x )	Bond 2	-0.85035	-0.85035	310300	rearo'n-	-0.85035
ancometere of o	Table 15.221. The MO to HO intercept geometrical bonu parameters of the E.	(eV)	Bond 1	-0.85035	-0.85035		-0.85035	-0.85035
4.	ometrical bonu	1000		1		-	ڻ	ځ:
	HO intercept go							
	1. The MO to			1	-	ن	ال الله	(.)
	Table 15.22	Bond			H-1)	)="HC"=()	) II ( ) ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II ( ) II	している

Table 15.222. The energy parameters (eV) of functional groups of naphthalene.

Parameters	C = C	CH Group	C – C Group
f	Group 0.75	1	1
$f_1$	2		
n ₁		1	1
$n_2$	0	0	0
$n_3$	0	0	0
$C_1$	0.5	0.75	0.5
$C_2$	0.85252	1	1
$c_1$	.1	1	1
$\mathcal{C}_2$	0.85252	0.91771	0.85252
$c_3$	0	1	0
c ₄ ·	3	1	2
c ₅	0	1	0
$C_{to}$	0.5	0.75	0.5
$C_{2\sigma}$	0.85252	1	1
$V_{u}$ (eV)	-101.12679	-37.10024	-34.43791
$V_{p}$ (eV)	20.69825	13.17125	10.26723
T (eV)	34.31559	11.58941	9.80539
$V_m$ (eV)	-17.15779	-5.79470	-4.90270
E(AOIHO) (eV)	0	-14.63489	-14.63489
$\Delta E_{_{H_{2}MO}}(_{AOIHO})$ (eV)	0	-1.13379	-1.13379
$E_T(AOIHO)$ (eV)	0	-13.50110	-13.50110
$E_T(H_2MO)$ (eV)	-63.27075	-31.63539	-31.63529
$E_T(atom-atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-0.56690
$E_{T}(MO)$ (eV)	-65.53833	-32.20226	-32.20226
$\omega \left(10^{15} \ rad \ / \ s\right)$	49.7272	26.4826	23.6343
$E_{\kappa}$ (eV)	32.73133	17.43132	15.55648
$\overline{\overline{E}}_{D}^{n}$ $(eV)$	-0.35806	-0.26130	-0.25127
$\overline{\overline{E}}_{Kvib}$ $(eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.12312 [2]
$\overline{E}_{osc}$ (eV)	-0.25982	-0.08364	-0.18971
$E_{mag}$ (eV)	0.14803	0.14803	0.14803
$E_{T}(Group)$ $(eV)$	-49.54347	-32.28590	-32.39198
$E_{initial}(c_A AO/HO) (eV)$	-14.63489	-14.63489	-14.63489
$E_{mittal}(c_5 AO/HO) (eV)$	0	-13.59844	0
$E_{D}(Group)$ (eV)	5.63881	3.90454	3.12220

Name 20' 20' 30' 30' 30' 1 (a' ₀ ) 2.62936 2.62936				Exp. θ (°)	119.4		,	120 [20-22]	(penzene)	120 [50-52]	(benzene)
C = C   CH   Group   Figure   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float   Float				g ©	119.40	+	120.30		61.021		18.811
C = C   CH   Group   Load bond and lease   Error			}	(0,2							
10   8   1   10   10   10   10   10				(e)			119.40				120.19
10   8   1   10040				e (o)							
C = C   CH   Group   100   1001   2010   1000   1001   1001   1001   1001   1001   1001   1001   1001   1001   1001   1001   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1000   1				$E_T$ (eV)	-1.85836				-1.85836		
10   8   1   10   10   10   10   10				<i>'</i> 3'	0.79232				0.79232		
C = C   C				5	-				~	-	
C = C   C				ű,	-				-		
C = C				U	-						
C = C		130		G2 Atom 2	0.79232				0.79232		
10   8   CF   CF   Green	- 1	- 1	خے	C ₂	0 79232				0.79232		
10   8   CF   CF   Green	Total Dolla Elletsy (eV)	90,79143	ım – atom, msp³.40	Atom 2 Hybridization Designation	(Table 13,3,A)	;		-	34		
10   8   CF   CF   Green	I otal bond Energy (eV)	90,74658	$E_r$ is $E_r$ (ato	Econtamble Atom 2	8107171	200			-17,17218		
Formula   Name   C = C   C   H		-	nental values [1].	Atom 1 Hybridization Designation	(Table 15.3.A)	10			34		
Formula   Name   C=C	H	8	ınd experim	E Confembre	0.00	-17.17210			-17,17218		
Formula   Name   C=C	Ú		nthalene a	2c' Terminal Atoms	) P	585			4.5585		
Formula   Name	C=C	01	rs of nap	2c' Bond 2 (u ₀ )		2.65034		1	2,62936		
Formula Name  CapRe Naphthalene  Table 15.224. The bond ang  Atums of Auge  Acc, C, C, C, H  Acc, C, H  Acc, C, H  CAC, CC  (aromatic)  ACC, CH  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  ACC, CC  AC			le naramete	2c' Bond I (a ₀ )		2.62936			2,62936		
Formula Chelle Table		Naphthalene	15 224 The hand ang	Aluns of Angle			H"2"2777	(naphthalene)	77,77	(aromatic)	HD:D7
	Formula	CoHe	Table								<u></u>

# **TOLUENE**

Toluene has the formula  $C_7H_8$  and comprises the benzene molecule with one hydrogen atom replaced by a methyl group corresponding to a  $CH_3$  functional group and a C-C functional group. The aromatic C = C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The  $CH_3$  functional group is the same as that of continuous and branched-chain alkanes given in the corresponding sections.

The bond between the methyl and aromatic ring comprises a C-C functional group that is are solved using the same principles as those used to solve the alkane functional groups wherein the 2s and 2p AOs of each C hybridize to form a single  $2sp^3$  shell as an energy 10 minimum, and the sharing of electrons between two  $C2sp^3$  HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. To match energies within the MO that bridges methyl and aromatic carbons, E(AO/HO) and  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.41) are -15.35946~eV (Eq. (14.155)) and  $\frac{-1.13379~eV}{2}$ , respectively.

To meet the equipotential condition of the union of the aromatic and methyl  $C2sp^3$  HOs of the C-C single bond, the parameters  $c_1$ ,  $C_2$ , and  $C_{2o}$  of Eq. (15.42) are one for the C-C group,  $C_{1o}$  and  $C_1$  are 0.5, and  $c_2$  given by Eq. (13.430) is  $c_2(C2sp^3HO) = 0.91771$ . To match the energies of the functional groups,  $E_T(atom-atom,msp^3.AO)$  of the C-C-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is -1.13379~eV which is the same energy per  $C2sp^3$  HO as that of the replaced C-H group.

The symbols of the functional groups of toluene are given in Table 15.225. The corresponding designation of the structure is shown in Figure 63. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of toluene are given in Tables 15.226, 15.227, and 15.228, respectively. The total energy of toluene given in Table 15.229 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.228 corresponding to functional-group composition of the molecule. The bond angle parameters of toluene determined using Eqs. (15.79-15.108) are given in Table 15.230.

	(a ₀ )	0,15511	0.55533		0,25279		0.37901		
	(a) (a)	1.20367	\$2054.0		1.68807		1.81430		
	er ©	45.13		28.98	34.97		28.27		
	6 D	101.11		45.76	105.69	100.00	118.44		
;	(°)	79.89	76.41	134.24		23.38	95.19		
	$E(C2sp^3)$ (eV)	-15.20178	16.90248	-16.90248		-15.20178	16 90747	10.500	
	$\frac{E_{Coulom}\{C2xp^2\}}{(eV)}$ Final	-15.39265	-17.09334	-17.09334		-15,39265		-17.09334	
	'freed (a ₀ )	1 79 1	0.79597	0.79597		0.88392		0.79597	
	fush d	17716.0	17719.0	17716.0		17716.0		0.91771	
	Final Total Energy	(eV) (eV) -(52.18259	-153.88327	-153.88327		152 18259		-153.88328	
	$\frac{18p^3AO}{f_T}$	Bond 4	, 0	-	>		0	٥	
	is $E_T$ atom $-$ atom, $mxp^3$ $AO$ .	Bond 3	-0,56690		-0,56690		0	0.05035	-0.0201-
1.27295	luene. $E_T$ is $E_T$	(eV) Bond 2	0 85035		-0.85035		0		-0.85035
1.47774	Table 15,227. The MO to HO intercept geometrical bond parameters of toluene. $E_T$ if Atom $E_T$	(eV) Bond 1	-0.56690	-0,85035	-0.85035		0.56690		-0.56690
++	metrical bond		U"		<i>ن</i> د	<b>,</b>	υ [†]		ປ້
1,22265	O intercept geo								
0.66540	7. The MO to F		H,	(H	•	ر. ريار.	H 1	6,1,3	-C,H,
$(A)$ $h_{,C}(a_{a})$	Table 15,227	Bond	$C-H\left(C_3H_3\right)$	C-H (C,H)	C = HC	C=(H,C,C)	2. 3.	(=)(,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	$\left  \left( C = \right) C_t - C_r H_s \right $

1.11 (avg.) (toluene)

> 1.524 (toluene) 1.47774

1.11 (avg.) (toluene) 1.22265

1,10974

1,51904

1,09327

 $\begin{array}{c} a \left( a_o \right) \\ c^* \left( a_o \right) \\ Sond Length \\ 2c^* \left( A \right) \\ Exp. Bond \\ Length \\ \left( A \right) \end{array}$ 

Table 15.226. The geometrical bond parameters of tolurne and experimental values [1].

CH (i) Group

> C=C Oroup 1.47348

C = C C + (i) C - C C - H C - H

CH (aromatic) (',  $-C_{\mathfrak{p}}$  ( $CH_{\mathfrak{f}}$  to aromatic bond)

CH, group

CC (aromatic bond)

Table 15.225. The symbols of functional groups of toluene.

Group 1,64920 1,04856

2.06004

1,60061

131468

Table 15.228. The energy parameters (eV) of functional groups of toluene.

		ronal groups of	, , , , , , , , , , , , , , , , , , , ,	<del></del>
Parameters	C = C Group	CH (i) Group	C – C Group	CH ₃ Group
$f_1$	0.75	1		Gloup
$n_{\rm l}$	2	1	1	3
$n_2$	0	0	0	2
$n_3$	0	0	0	0
$C_1$	0.5	0.75	0.5	0.75
$C_2$	0.85252	1	1	1
$c_1$	1	1	1	1
$c_2$	0.85252	0.91771	0.91771	0.91771
	0	1	0	0
<i>c</i> ₄	3	1	2	1
$c_{s}$	0	. 1	0	3
C _{lo}	0.5	0.75	0.5	0.75
$C_{2o}$	0.85252	1	1	1
$V_{u}(eV)$	-101.12679	-37.10024	-29.95792	-107.32728
$V_{p}(eV)$	20.69825	13.17125	9.47952	38.92728
T(eV)	34.31559	11.58941	7.27120	32.53914
$V_m$ (eV)	-17.15779	-5.79470	-3.63560	-16.26957
E(AOIHO) (eV)	0 .	-14.63489	-15.35946	-15.56407
$\Delta E_{H_2MO}(AOIHO)$ (eV)	0	-1.13379	-0.56690	0
$E_{T}$ (логно)· (eV)	0 .	-13.50110	-14.79257	-15.56407
$E_{T}(H_{2}MO)$ (eV)	-63.27075	-31.63539	-31.63537	-67.69451
$E_{r}(atom-atom, msp^{3}.AO)$ (eV)	-2.26759	-0.56690	-1.13379	0
$E_{_T}(MO)$ (eV)	-65.53833	-32.20226	-32.76916	-67.69450
$\omega \left(10^{15} \ rad \ / \ s\right)$	49.7272	26.4826	16.2731	24.9286
$E_{\kappa}$ (eV)	32.73133	17.43132	10.71127	16.40846
$\overline{E}_{_{ m D}}$ (eV)	-0.35806	-0.26130	-0.21217	-0.25352
$\overline{E}_{_{K\!v\!i\!b}}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.14940 [53]	0.35532 (Eq. (13.458))
$\overline{E}_{oxc}$ $(eV)$	-0.25982	-0.08364	-0.13747	-0.22757
$E_{mag}$ (eV)	0.14803	0.14803	0.14803	0.14803
$E_{T}(Group) (eV)$	-49.54347	-32.28590	-32.90663	-67.92207
$E_{initial}(c_4 AO/HO) (eV)$	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_s AO/HO) (eV)$	0	-13.59844	0	-13.59844
$E_{D}(Group)$ (eV)	5.63881	3.90454	3.63685	12.49186
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					$E_{7}$ (eV)			-1.85836	
					ۍ.		7	0.79232	
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compared t	ergy R	0			C ₂ Aloin 2		0 79737		
able 13.228 c	Experimental Total Bond Energy (eV)	69.546			C ₂ Atom I		0.79232		
nine energies of 1	Calculated Total Bond Energy (eV)	69.48425	om, msp³.AO).	Atom 2	Hybridization Designation	(Table 15.3.A)	34		
TIL TOSITION AN	CH ₃	_	$E_T(atom - at$	2	Cratambe Aloin 2		-17.17218		
Every compared to the experimental values of Table 13.228 compared to the experimental values [7]	C'-C' Group		values [1]. $E_T$ is	Atom I	Hybridization Designation	(Table 15.3.A)	34		
	- 1		perimental	3	Atom [		-17.17218		
	Œ,	^	ne and exp	2c,	Tenuinal Aluns (a,)		4.5585	Ī	•
	$C = C \qquad CH \text{ (i)}$		s of tolue	2c'	(a ₀ )		2.62936		
			le parameter	2c,	(a)		2,62936 2,62936 4,5585		
	la Name		Table 15.230. The bond angle parameters of toluene and experimental values [1]. $E_r$ is $E_r$ (atom – atom, mxp ² .AO).	Alonus of Angle		33.11	(aromatic)	H.J.17	(aromatic)
	Formula C.H.		Table						_

# **CHLOROBENZENES**

Chlorobenzenes have the formula  $C_6H_{6-m}Cl_m$  and comprise the benzene molecule with at least one hydrogen atom replaced by a chlorine atom corresponding to a C-Cl functional group. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section.

The small differences between energies of ortho, meta, and para-dichlorobenzene is due to differences in the energies of vibration in the transition state that contribute to  $E_{osc}$ . Two types of C-Cl functional groups can be identified based on symmetry that determine the parameter R in Eq. (15.48). One corresponds to the special case of 1,3,5 substitution and 10 the other corresponds to other cases of single or multiple substitutions of Cl for H. P-dichlorobenzene is representative of the bonding with R=a. 1,2,3-trichlorbenzene is the particular case wherein is R=b. Also, beyond the binding of three chlorides  $E_{mag}$  is subtracted for each additional Cl due to the formation of an unpaired electrons on each C-Cl bond.

The bond between the chlorine and aromatic ring comprises two C-Cl functional groups that are solved using the same principles as those used to solve the alkyl chloride functional groups as given in the corresponding section wherein the 2s and 2p AOs of each C hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and Cl AO to form a MO permits each participating hybridized 20 orbital to decrease in radius and energy. As in the case of alkyl chlorides,  $c_2$  of Eq. (15.52) for each C-Cl-bond MO is one, and the energy matching condition is determined by the  $C_2$  parameter given by Eq. (15.111) which is  $C_2\left(C2sp^3HO\ to\ Cl\right)=0.81317$ . To match energies within the MO that bridges the chlorine AO and aromatic carbon  $C2sp^3$  HO,  $E\left(AO/HO\right)$  and  $\Delta E_{H_2MO}\left(AO/HO\right)$  in Eq. (15.42) are  $-14.63489\ eV$  and  $-2.99216\ eV$ , 25 respectively. The latter matches twice that of the replaced C-H-bond MO plus  $E_T\left(atom-atom,msp^3.AO\right)$ . To match the energies of the functional groups,  $E_T\left(atom-atom,msp^3.AO\right)$  of the C-Cl-bond MO in Eq. (15.53) due to the charge donation from the C and Cl atoms to the MO is  $-0.72457\ eV$  (Eq. (14.151)).

The symbols of the functional groups of chlorobenzenes are given in Table 15.231. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of chlorobenzenes are given in Tables 15.232, 15.233, and 15.234, respectively. The total energy of each 5 chlorobenzene given in Table 15.235 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.234 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of chlorobenzenes 10 determined using Eqs. (15.79-15.108) are given in Table 15.236.

Table 15.231. The symbols of functional groups of chlorobenzenes.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH (i)
Cl-C ( $Cl$ to aromatic bond)	C-Cl (a)
Cl - C (Cl to aromatic bond of 1,3,5-trichlorbenzene)	C – Cl (b)

760	;			•			PC	<b>T</b> /1	US:	<b>2</b> 006/	0426	92		<u>روس</u> ا ا	8.44. 1
$C_k = (CI)C_s = C_k$ $(C_k \text{ bound to } H \text{ or } CI)$	C = C' - C'	$\left(C=\right)_{2}C-CI$	$C = HC_k = C$	(-H')		5010	Table 15.233. The Mo	e	$h_*c\left(a_0\right)$	Exp. Bond Length (A)	Bond Length 2c' (A)	c' (a ₀ )	$a\left(a_{\scriptscriptstyle 0}\right)$	Parameter	Table 15.232. The ge
							Table 15.233. The MO to HO intercept geometrical bond parameters of chlorobenzenes. $E_r$ is $E_r$ ( $atom-atom, ansp^3$ . $AO$ )	0.89223	0.66540	1.400 (chlorobenzene)	1.39140	1.31468	1.47348	C=C	Table 15.232. The geometrical bond parameters of chlorobenzenes and experimental values []
رئ ا	a	٠,	٠,	,:	to 1%	Atom	etrical bon	0.	-	(chlor	1:			00	ters of chlo
-0.36229	-0.36229	-0.36229	-0.85035	-0.85035	(eV) Bond I	E _T	d parameters c	0.64537	1.22265	1.083 (chlorobenzene)	1.09327	1.03299	1.60061	CH (i)	robenzenes an
-0.85035	. 0	-0.85035	-0.85035	-0,85035	(eV) Bond 2	$E_T$	of chlorobenzenes.	0.74630	1.46967	1.737 (chlorobenzene)	1.74397	1.64782	2.20799	('−(') (a) Group	d experimental va
-0.85035	0	-0.85035	-0.56690	-0.56690	(eV) Bond 3	$E_T$	$E_T$ is $E_T$								lues [1].
.0	0	0	0	. 0	(eV) Bond 4	$E_{r}$	atom – atom, msp³.	0.74630	1.46967	1.737 (chlorobenzene)	1.74397	1.64782	2.20799	C-Cl (b) Group	
-153.67867		-153,67867	-153.88327	-153.88327	(2.5p ³ )	Final Total	<i>40</i> ).								
0.91771	1.05158	0.91771	0,91771	0.91771	(a ₀ )	Fastind									

(a₀)
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0.80561

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38.84 58.98 31.67

45.35

0.56614

37.22

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(°)

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Parameters	$C \stackrel{3e}{=} C$	CH (i)	C-Cl (a)	C-Cl (b)
6	Group	Group	Group	Group
$f_1$	0.75	1		
n ₁	2	1	1	1
<i>n</i> ₂	0 .	0	0	0
<i>n</i> ₃	0	0	0	0
C _i	0.5	0.75	0.5	0.5
$C_2$	0.85252	1	0.81317	0.81317
$c_{\scriptscriptstyle 1}$	1	1	1	1
$c_{2}$	0.85252	0.91771	1	1
$c_3$	0	1	. 0	0
$c_4$	3	1	2	2
<i>c</i> ₅	0	1	0	0
$C_{1o}$	0.5	0.75	0.5	0.5
$C_{2o}$	0.85252	1	0.81317	0.81317
$V_e(eV)$	-101.12679	-37.10024	-31.85648	-31.85648
$V_p(eV)$	20.69825	13.17125	8.25686	8.25686
T (eV)	34.31559	11.58941	7.21391	7.21391
$V_m$ (eV)	-17.15779	-5.79470	-3.60695	-3.60695
E(логно) (eV)	0	-14.63489	-14.63489	-14.63489
$\Delta E_{H_2MO}$ (AOIHO) (eV)	0	-1.13379	-2.99216	-2.99216
$E_{T}(AOIHO)$ (eV)	0	-13.50110	-11.64273	-11.64273
$E_T(H_2MO)$ (eV)	-63.27075	-31.63539	-31.63539	-31.63539
$E_T(atom-atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-0.72457	-0.72457
$E_T(MO)$ (eV)	-65.53833	-32.20226	-32.35994	-32.35994
$\omega \left(10^{15} \ rad \ / \ s\right)$	49.7272	26.4826	8.03459	14.7956
$E_K$ (eV)	32.73133	17.43132	5.28851	9.73870
$\overline{E}_{D}$ (eV)	-0.35806	-0.26130	-0.14722	-0.19978
$\overline{E}_{Kvib}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.08059 [12]	0.08059 [12]
$\overline{E}_{asc}$ (eV)	-0.25982	-0.08364	-0.10693	-0.15949
$E_{mag}$ (eV)	0.14803	0.14803	0.14803	0.14803
$E_{T}(Group)$ (eV)	-49.54347	-32.28590	-32.46687	-32.51943
$E_{minal}(c_s \text{ AOIHO}) (eV)$	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_s AOIHO) (eV)$	0	-13.59844	0	0
$E_{D}(Group)$ (eV)	5.63881	3.90454	3.19709	3.24965

of the  $E_{D}(\omega_{mq})$  (eV) values based on composition is given by (15.58). Table 15.235. The total bond energies of chlorobenzenes calculated using the functional group composition and the energies of Table 15.234 compared to the experimental values [2]. The magnetic energy  $E_{\rm exp}$  that is subtracted from the weighted sum

נימי נימי	2	2011	2 5	2 2	1.011IIIII	1	
Hexachlorobenzene	1,5,0-memorocazare	II Tarichlombenzene	Cilionopenzene	Chiambanana	148116	Name	
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0	w ·	w	<b>.</b>	S	3	$CH \oplus$	
6		w	2	-	Group	( -(./(2)	14 15 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
0	_	0	0	0	Group	(a) (b)	C-11 (A)
3	0	0	0	0		gun, 2	77
52.57130	55.29542	55,13773	55.84518	56,55263	Energy (eV)	Total Bond	Calculated
52,477	55,255	55.077	55.852	56.581	(eV)	Total Bond Energy	Experimental
-0.00179	-0.00073	-0.00111	0.00012	0.00051	til.	Fron	Delative

<del></del>		<del></del> 1.	
7CCCH 7CCH	ZCCC (aromatic)	Atoms of Angla	Table 15.236. The bond angle parameters of chlorobenzenes and experimental values [1]. $E_r$ is $E_r(atom-atom,msp^3.AO)$
	2.62936	$\frac{2c'}{18\text{end }1}$ $(a_n)$	ond angle pa
	2.62936	2c' Hond 2 (a _e )	rameters o
	4.5585	2c' Tenuisal Atoms (a _n )	f ciılorobe
	-17.17218	Erenlenke Atom !	nzenes and o
٠	34	Atom I Hybridization Designation (Table 15.3.A)	experimental values
	-17.17218	E _{Callombye} Atom 2	$s[1]$ . $E_T$ is
	34	Atom 2 Hybridization Designation (Table 15.3.A)	$E_{\tau}$ (atom – atom, ms
	0.79232	C ₂ Atem 1	p'.AO).
	0.79232	C ₂ Alom 2	
*	-	c,	
	tent .	. 2	
	-	c ₁	
	0.79232		
	-[.85836	E _r (eV)	
		(°)	
120.19		(°)	
		© 20	
119.91	120.19	Cal. θ (°)	
120 [50-52] (benzene)	(∠CC(H)C chlorobenzene) 121.7 (∠CC(CI)C chlorobenzene) 120 [50-52] (benzene)	Exp. θ (°)	

## PHENOL

Phenol has the formula  $C_6H_6O$  and comprises the benzene molecule with one hydrogen atom replaced by a hydroxyl corresponding to an OH functional group and a C-O functional group. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The OH functional group is the same as that of alcohols given in the corresponding section.

The bond between the hydroxyl and aromatic ring comprises a C-O functional group that is are solved using the same principles as those used to solve the alcohol functional groups wherein the 2s and 2p AOs of each C hybridize to form a single  $2sp^3$  10 shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and O AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. In aryl alcohols, the aromatic  $C2sp^3$  HO has a hybridization factor of 0.85252 (Eq. (15.143)) with an initial energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)) and the O AO has an energy of  $E(O) = -13.61806 \, eV$ . To meet the equipotential condition of the union of the C-O  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the C-O-bond MO given by Eqs. (15.68) and (15.70) is

$$c_{2}(arylC2sp^{3}HO \ to \ O) = \frac{E(O)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$

$$= \frac{-13.61806 \ eV}{-14.63489 \ eV}(0.85252)$$

$$= 0.79329$$
(15.150)

 $E_T(atom-atom, msp^3.AO)$  of the C-O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is  $-1.49608\,eV$ . It is based on the energy 20 match between the OH group and the  $C2sp^3$  HO of an aryl group and is given by the linear combination of  $-0.92918\,eV$  (Eq. (14.513)) and  $-1.13379\,eV$  (Eq. (14.247)), respectively.

The symbols of the functional groups of phenol are given in Table 15.237. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of phenol are given in Tables 15.238, 15.239, and 15.240, respectively. The total energy of phenol given in Table 15.241 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.240

corresponding to functional-group composition of the molecule. The bond angle parameters of phenol determined using Eqs. (15.79-15.108) are given in Table 15.242.

Table 15.237. The symbols of functional groups of phenol.

5

Functional Group	Group Symbol
CC (aromatic bond)	$C \stackrel{3e}{=} C$
CH (aromatic)	<i>CH</i> (i)
Aryl C-O	C-O (a)
OH group	OH

Table 15.238. The geometrical bond parameters of phenol and experimental values [1].

Parameter	C = C Group	CH (i) Group	C−O (a) Group	OH Group
$a\left(a_{0}\right)$	1.47348	1.60061	1.68220	1.26430
$c'(a_0)$	1.31468	1.03299	1.29700	0.91808
Bond Length $2c'(A)$	1.39140	1.09327	1.37268	0.971651
Exp. Bond Length (Å)	1.397 avg. (phenol)	1.084 (phenol)	1.364 (phenol)	0.956 (phenol)
$b,c(a_0)$	0.66540	1.22265	1.07126	0.86925
е	0.89223	0.64537	0.77101	0.72615

10010 12:1202. The last of the interests Beautiful and beautiful and the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last of the last	de Goomatian oc	the parameters of	- Les second												
Bond	Atom	1:	$L_{\mathcal{J}}$	$E_T$	$E_{T}$	Final Total	ranted.	r finet	Ec., (C'2sp3)	$E(C2sp^3)$	θ	θ.	·,e	<i>a</i> -	<i>d</i>
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C'2sp³ (eV)	(a _s )	$(a_{\scriptscriptstyle \mathrm{D}})$	(eV) Final	(eV) Final	(°)	(°)	(°) 	$(a_p)$	$(a_0)$
C-H(C,H)	ئ د	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16,90248	74.42	105.58	38.84	1.24678	0.21379
$\left(C_{h}^{2}\right) C_{h}O - H$	0	-0,74804	o	0	Đ		1,00000	0.87363	-15.57379		115.79	64.21	64.82	0.53799	0.38009
$\left(C_{*}^{*}\right)^{*}C_{*}^{*}-OH$	<i>c</i> .	-0.74804	-0.85035	-0.85035	0	-154,06442	0,91771	0.78762	-17.27448	-17.08362	100.00	80.00	46.39	1.16026	0.13674
$HO^{-n}$ , $\frac{1}{n}$	0	-0.74804	5	o	0		00000.1	0.87363	15.57379		106.51	73.49	51.43	1,04871	0.24829
$C_{x}^{+}$ $C_{x}^{+}$	<i>(</i> .	-0.74804	-0.85035	-0.85035	0	~154,06442	0.91771	0.78762	-17.27448	-17.08362	133.88	46.12	58.55	0.76870	0.54598
$= \left( \frac{1}{2} \left( \frac{1}{2} \left( \frac{1}{2} \right) \right) C_{0}^{*} O H \right)$	Ĉ.	-0.85035	-0,85035	-0.56690	0	-153,88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.240. The energy parameters (eV) of functional groups of phenol.

Table 15.240. The energy parameter Parameters	C = C	CH (i)	C-O (a)	<i>OH</i> Group
	Group	Group	Group	Group
$f_{I}$	0.75	1		<del></del>
$n_{_{\mathrm{i}}}$	2	1	1	1
$n_2$	0	0	0	0
$n_3$	0	0	0	0
$C_1$	0.5	0.75	0.5	0.75
$C_2$	0.85252	1	l	1
$C_{i}$	1	1	1	0.75
$c_2$	0.85252	0.91771	0.79329	1
<i>C</i> ₃	0	1	0	1
$C_4$	3	1	2	1
$c_5$	0	1	0	1
$C_{lo}$	0.5	0.75	0.5	0.75
C ₂₀ · · · · · · · · · · · · · · · · · · ·	0.85252	. 1 .	1	1
$V_{e}(eV)$	-101.12679	-37.10024	-34.04658	-40.92709
$V_{p}(eV)$	20.69825	13.17125	10.49024	14.81988
T(eV)	34.31559	11.58941	10.11966	16.18567
$V_m$ (eV)	-17.15779	-5.79470	-5.05983	-8.09284
E(логно $)$ $(eV)$	0	-14.63489	-14.63489	-13.6181
$\Delta E_{H_2MO}$ (AOIHO) (eV)	0	-1.13379	-1.49608	0
$E_{T}$ (логно) (eV)	0	-13.50110	-13.13881	-13.6181
$E_T(H_2MO)$ (eV)	-63.27075	-31.63539	-31.63532	-31.63247
$E_T(atom-atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-1.49608	0
$E_{T}(MO)$ (eV)	-65.53833	-32.20226	-33.13145	-31.63537
$\omega \left(10^{15} \ rad \ / \ s\right)$	49.7272	26.4826	13.3984	44.1776
$E_{\kappa}$ (eV)	32.73133	17.43132	8.81907	29.07844
$\overline{E}_{D}(eV)$	-0.35806	-0.26130	-0.19465 ·	-0.33749
$\overline{E}_{Kvib}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.12808 [19]	0.46311 [17-18]
$\bar{E}_{osc}$ (eV)	-0.25982	-0.08364	-0.13061	-0.10594
$E_{mag}$ (eV)	0.14803	0.14803	0.14803	0.11441
$E_T(Group)$ (eV)	-49.54347	-32.28590	-33.26206	-31.74130
Eminal (c. AOIHO) (eV)	-14.63489	-14.63489	-14.63489	-13.6181
$E_{initial}(c_s AOIHO) (eV)$	0	-13.59844	0	-13.59844
$E_{D}(Group)$ (eV)	5.63881	3.90454	3.99228	4.41035

Formula Name		2=C C=C	(H (I)	) (i)	C=C ('H (i) ('-() {a}) (IH Calculated Experimental Relative C=C ('H (i) Group Group Engy (e4) GeV) Error 6 5 } { 61.7847 61.784 Angue (24) Angue 7	OH Group	Calculated Total Bond Energy (eV) 61 75817	Experimental  Total Bond Energy  (eV)	Agi.	Relative Emor		5							
CaH4O Phonol		5		5	~	~	61.75817	61.704	è	-0,00087									
Table 15.242. The bond angle parameters of phenol and experimental values [1]. $E_r$ is $E_r \{ann-ann, nsp, 30\}$	ngle paramet	ers of phe	nol and e	perimental (	values [1]. $E_r$ is	E _r {aiom – air	om,msp'AO}.												
Atoms of Angle	$\frac{2c'}{(a_b)}$	$\frac{2e'}{Rand2}$	2c' Yemund Atoms	E sudante	Atom 1 Hibridization Designation	L'intermète Assess 2	Atom 2 Hybridization Designation	C ₂	c.	£.	5	"L	'SV	E _V (eV)	(°, 6)	(0)	(0,0	(°)	(°)
(aromatic)	2,62936	2,62936	4.5585	4.5585 -17.17218	34	-17,17218	Ħ	0.79232	0.79232	-	-	-	0.79232	-1.85836			$\perp$	120.19	92,1
(aromatic)																120.19	_	119,91	120 [50-5
11.00						-										_	_	_	(ber

### ANILNE

Aniline and methyl aniline have the formula  $C_6H_7N$  and  $C_7H_9N$ , respectively. They comprise the benzene and toluene molecules with one hydrogen atom replaced by an amino group corresponding to an  $NH_2$  functional group and a C-N functional group. The 5 aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The C-C and  $CH_3$  functional groups of methyl anilines are equivalent to those of toluene given in the corresponding section.

The aryl amino  $(NH_2)$  functional group was solved using the procedure given in the Dihydrogen Nitride  $(NH_2)$  section. Using the results of Eqs. (13.245-13.368), the aryl amino parameters in Eq. (15.51) are  $n_1=2$ ,  $C_1=0.75$ ,  $C_2=0.93613$  (Eqs. (13.248-13.249)),  $C_{1o}=1.5$ , and  $c_1=0.75$ . In the determination of the hybridization factor  $c_2$  of Eq. (15.52) for the N-H-bond MO of aryl amines, the  $C2sp^3$  HO of the  $C-NH_2$ -bond MO has an energy of  $E(C,2sp^3)=-15.76868~eV$  (Eq. (15.18) corresponding to s=2 in Eqs. (15.18-15.20), and the N AO has an energy of E(N)=-14.53414~eV. To meet the equipotential condition of the union of the N-H  $H_2$ -type-ellipsoidal-MO with the  $C2sp^3$  HO, the hybridization factor  $c_2$  given by Eq. (15.68) is

$$c_2(H \text{ to anline } N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.76868 \text{ eV}} = 0.92171$$
 (15.151)

The bond between the amino and aromatic ring comprises a C-N functional group that is the same as that of  $2^{\circ}$  amines (methylene) except that the energies corresponding to oscillation in the transition state are those of aniline. The group is solved using the same principles as those used to solve the primary and secondary-amine functional groups wherein the 2s and 2p AOs of each C hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and N AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. The 25 hybridization is determined in a similar manner to that of the C-O group of phenol. In anilines, the aromatic  $C2sp^3$  HO has a hybridization factor of 0.85252 (Eq. (15.143)) with an initial energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)) and the N AO has an energy

of  $E(N) = -14.53414 \ eV$ . To meet the equipotential condition of the union of the C-O  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.51) for the C-O-bond MO given by Eqs. (15.68) and (15.70) is

$$c_{2}(arylC2sp^{3}HO \ to \ N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$

$$= \frac{-14.53414 \ eV}{-14.63489 \ eV}(0.85252)$$

$$= 0.84665$$
(15.152)

- 5  $E_T(atom-atom, msp^3.AO)$  of the C-N-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is  $-1.13379 \, eV$  (Eq. (14.247)). It is based on the energy match between the  $NH_2$  group and the  $C2sp^3$  HO of the aryl group and is twice that of the aryl C-H group that it replaces.
- The symbols of the functional groups of aniline and methyl-substituted anilines are given in Table 15.243. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aniline and methyl-substituted anilines are given in Tables 15.244, 15.245, and 15.246, respectively. The total energy of each aniline and methyl-substituted aniline given in Table 15.247 was calculated as the sum over the integer multiple of each  $E_D$  (Group) of Table 15.246 corresponding to functional-group composition of the molecule. The bond angle parameters of aniline and methyl-substituted anilines determined using Eqs. (15.79-15.108) are given in Table 15.248.

20 Table 15.243. The symbols of functional groups of aniline and methyl-substituted anilines.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH (i)
Aryl C-N	C-N (a)
NH ₂ group	$N\!H_2$
$C_a - C_h$ ( $CH_3$ to aromatic bond)	C-C (a)
CH₃ group	$C-H$ $(CH_3)$

		1		Γ		Γ		~		_		Γ			}	
1100	(-H (CH)	Group	1.64920	100	1.04850		1 10074	1.101.1		111 (200	(toluene)	AUCTE 1	1.6627	0.63580		
tai values [1].	(a) (a)	Group	2.06004		1,43528		,001.	+061 c.1		1 524	(toluene)		1,477/4	C 50572	1,020,0	
ilines and experimen	NH,	Group	1 34428	1,477	0.04134	U.T.I.		0.99627			0.998 (aniline)		0.81370		0.75055	
methyl-substituted an	C ~ N (a)	Group	6,5,6,	1.8/155	10310	1.34393		1,42449			1.431 (aniline)		121254		0.74297	
1 Land received of aniline and methyl-substituted anilines and experimental values [1]	Car to	C us	dinis.	1,60061		1.03299		1,09327			1.084		390063	1.6222	0.64537	
grand page	eomemical bollu para	C=C Group			1,31468	-	1 39140	24:		1,397 avg.	(piletini)		0.66540	0.89273	0.07443	
1	Table 15.244, The H	Parameter a (a.)		(0)	(a)	/= /	Bond Length	2c' (A)	,	Exp. Bond Length	3		b.c [a]	/ / /	9	

7,	(a°)	0,21375	1551.0	(1,1 ₂ )	0.46500	1	0,0210	+	5,00,0	+	0.2527	+	0.3790	+		0.555		-	
a'	$\{a_o\}$	1.24678		1,2056/	0.47634		1.36696		1.24859	-	1,68807		1.81430	$\frac{1}{1}$		0,75935			
θ,	©	38.84		43.13	67 79		41,01		46,43	-	74.97		78.27			58.98			
9	( <u>0</u> )	105 59	arroll	101.11	20.05	OP.AN	15.18		83.68		106.62		200 44			45.76			
ıθ	©	5	74:47	79.89		121.74	88.49		96.32		£		1	91.30		134.74			
El Cosmi)	(eV) Final		-16.90248	-15.20178			16 00748				921023	#/107°C1-		-16.90247		26,000.21	-10,20446		
(C250*)	Final Co.	1	-17,09334	-15 39265		-15.39265	1000000	+000011-	\$9201.51-			-15.39265		-17.09334			-17.09534		
_	(a) (a)		0 79597	COERK	,	0.88392		0.79597	L0509.8	765000		0.88392		76567.0			0.79597		
sp.At.j.	$\begin{pmatrix} a_o \\ a_o \end{pmatrix}$	1	17716.0	ittioo	1111670	0.93084		17716.0		0.93084	-	17716.0	1	0,91771			0,91771		
atom - atom, n	E, Final Total (eV) (eV) (C2p) (C2p) (C2p) (C2p)			-152.18259			-153,88328				-152,18259		-153.88328			-153.88327			
nes. E _T is E _T			+	=	•	1	0		8		0		0			8			
substituted anili	(eV)	c pung	-0.56690		0	=	;	-0.85035		0	1	0		-0,85035			-0.56690		
of aniline and methyl-substituted anilines. $E_T$ is $E_T(atom-atom,msp.At.)$ .	E, (eV)	Bond 2		-0, K5055	0	-	-	-0,85035	1	٥				-0.85035		-0.85035			
trameters of ani	Er (eV) (e Bond I Ba		-0.56696		-0.56690	-0.56690	1	06995 07		00.252.00	-0.3607U	0.56690			0.85035		-		
etrical bond pa	Atom (1 B)			=	×		,	~~	*	;	ـــــ در°	,			ـــــــــــــــــــــــــــــــــــــ	 	ئر		
Lis 15 245 The MO to HO intercept geome	Table 15.245. The MO to HO intercept geometrical bond parameters			('-H (('H)	(17)	(-u') (-u')	$C_h = C_h N H - H$	4	( = ) ( " - MH ₂	(A	$\langle i_k = \langle i_n - NH_2 \rangle$	(2)	('=   (', - (', H';	27 /20	('=' (', ~(', H,	3c 3c 3c	1117 X	$C = (H^2N)C^* = C$	

Table 15.246. The energy parameters (eV) of functional groups of aniline and methyl-substituted anilines.

Parameters	C = C Group	CH (i) Group	C – N (a) Group	NH ₂ Group	C-C (a) Group	CH ₃ Group
$f_1$	0.75	1				
$n_{\parallel}$	2	1	1	2	1	3
$n_2$	0	0	0	0	0	2
$n_3$	0	0	0	1	0	0
C ₁	0.5	0.75	0.5	0.75	0.5	0.75
$C_2$	0.85252	1	1	0.93613	1	1
$c_{_{1}}$	1	1	1	0.75	1	1
<i>c</i> ₂	0.85252	0.91771	0.84665	0.92171	0.91771	0.91771
$c_3$	0	1	0	0	0	0
$c_4$	3	1	2	1	2	1
<i>c</i> ₅	0	1	0	2	0	3
$C_{lo}$	0.5	0.75	0.5	1.5	0.5	0.75
C ₂₀	0.85252	1	1	1	1	1
$V_{e}$ (eV)	-101.12679	-37.10024	-32.76465	-78.97795	-29.95792	-107.32728
$V_p$ (eV)	20.69825	13.17125	10.10870	28.90735	9.47952	38.92728
T (eV)	34.31559	11.58941	9.04312	31.73641	7.27120	32.53914
$V_m$ (eV)	-17.15779	-5.79470	-4.52156	-15.86820	-3.63560	-16.26957
E(логно $)$ $(eV)$	0	-14.63489	-14.63489	-14.53414	-15.35946	-15.56407
$\Delta E_{H_2MO}$ (ΛΟΙΗΟ) (eV)	0	-1.13379	-1.13379	0	-0.56690	0
$E_{T}$ (логно) (eV)	0	-13.50110	-13.50110	-14.53414	-14.79257	-15.56407
E(n, AOIHO) (eV)	0	0	0	-14.53414	0	0
$E_{T}(H_{2}MO)$ (eV)	-63.27075	-31.63539	-31.63549	-48.73654	-31.63537	-67.69451
$E_T(atom-atom,msp^3.AO)$ (eV)	-2.26759	-0.56690	-1.13379	0	-1.13379	0
$E_T(MO)$ (eV)	-65.53833	-32.20226	-32.76916	-48.73660	-32.76916	-67.69450
$\omega \left(10^{15} \ rad \ / \ s\right)$	49.7272	26.4826	11.9890	68.9812	16.2731	24.9286
$E_{\kappa}$ (eV)	32.73133	17.43132	7.89138	45.40465	10.71127	16.40846
$\overline{\overline{E}}_{D}$ (eV)	-0.35806	-0.26130	-0.18211	-0.42172	-0.21217	-0,25352
$\overline{E}_{Kvib}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.15498 [54]	0.40929 [22]	0.14940 [53]	0.35532 (Eq. (13.458))
$\widetilde{\widetilde{E}}_{osc}$ (eV)	-0.25982	-0.08364	-0.10462	-0.21708	-0.13747	-0.22757
$E_{mag}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{r}(Group)$ $(eV)$	-49.54347	-32.28590	-32.87379	-49.17075	-32.90663	-67.92207
$E_{inntol}(c_{i}$ AOIHO) (eV)	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489
Einitial (c, AOIHO) (eV)	0	-13.59844	0	-13.59844	0_	-13.59844
$E_D(Group)$ (eV)	5.63881	3.90454	3.60401	7.43973	3.63685	12.49186

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ond energies of aniline and methyl-substituted antlines calcu		ζ
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Table 15.247. The total bond ene		
ie 15		cjinu
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						Ë	120 (ber	120 (ber	l (an	
						Cal. θ (°)	120.19	16.91	113.89	02.001
						( ₀ )				
						(e)		120,19		
						(o) *e				
						$E_{7}$ (eV)	-1.85836		0	
Relative Error	-0.00093	0.00025	0.00050	0.00040		<i>''</i>	0,79232		1.06823	10101
						ษ	-		0.75	27.0
Total Bond Energy (eV)	64.374	76.643	76.661	76.654	ļ	2	-		-	
						ئ.	-		-	21.0
Total Bond Energy (eV)	64,433	76,623	76.623	76,623	m,msp³.AO)	C ₂ Atom 2	0,79232		-	0.86284
$CH_3$	0	-	-	_	$E_T(atom-ate$	C ₂ . Akom I	0.79232		0.93613 Eq. (13.248))	0.84665
C-C (a) Group	0	_	_	-	values [1]. $E_T$ is	Atom 2 Hybridization Designation (Table 15.3.A)	75	3	ж	
<i>NH</i> , Group	-			-	experimental	Erentosthe Mon 3	-17.17218		æ	10.000
C - N (a) Group	1	_	_	-	ituted anilines and	Atom I Hybridization Designation (Table 15.3 A)	34		z	;
(H (i)	5	7	-7	4	rethyl-subst	Erpekunhe Atom I	-17.17218		-14,53414	
Ü					ine and m	2c' Terminal Atoms (a ₀ )	4,5585		3,1559	
C = C	9	ų	S	9	ers of anili	2c' Bend 2 (a ₀ )	2.62936 2 62936 4.5585		1.88268 1.88268 3.1559	_
					sle paramet	2c' Houst I (a _n )	2.62936		1.88268	
Name	Aniline	2-methylaniline	3-methylaniline	4-methylaniline	Table 15.248. The bond angle parameters of aniline and methyl-substituted anilines and experimental values [1]. $E_T$ is $E_T(atom-atom,mxp^2,AO)$	Atoms of Anglo	ZCCC (aromatic)	Z( 'C'H (aromatic)	ZHNH.	
Formula	C,H,N	ZTU	CHN	CHN	Table 1					

### ARYL NITRO COMPOUNDS

Aryl nitro compounds have a hydrogen of an aryl group replaced by a nitro corresponding to an  $NO_2$  functional group and a C-N functional group. Examples include nitrobenzene, nitrophenol, and nitroanilne with formulas  $C_6H_5NO_2$ ,  $C_6H_5NO_3$ , and  $C_6H_6N_2O_2$ , respectively. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The OH and C-O functional groups of nitrophenols are the same as those of phenol given in the corresponding section. The  $NH_2$  and C-N functional groups of nitroanilines are the same as those of aniline given in the corresponding section. The differences between the total bond energies of the nitroanilines given in Table 15.252 are due to differences in the  $E_{oxc}$  term. For simplicity and since the differences are small, the  $E_{oxc}$  terms for nitroanilines were taken as the same.

The  $NO_2$  group is the same as that given in the Nitroalkanes section. The bond between the nitro and aromatic ring comprises a C-N functional group that is the same as 15 that of nitroalkanes given in the corresponding section except that  $E_T(atom-atom,msp^3.AO)$  is -0.72457~eV, one half of that of the C-N-bond MO of nitroalkanes and equivalent to that of methyl (Eq. (14.151)) in order to maintain the independence and aromaticity of the benzene functional group. In addition, the energy terms due to oscillation in the transition state correspond to those of an aryl nitro compound.

The symbols of the functional groups of aryl nitro compounds are given in Table 15.249. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aryl nitro compounds are given in Tables 15.250, 15.251, and 15.252, respectively. The total energy of each aryl nitro compound given in Table 15.253 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.252 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of aryl nitro compounds determined using Eqs. (15.79-15.108) are given in Table 15.254.

nal groups of aryl nitro compounds.  Group Symbol	C = C $CH$ (i)	C-N(a)	C-N (b)	C-O (a)	$NO_2$	$NH_2$	НО	
Table 15.249. The symbols of functional groups of aryl nitro compounds.  Functional Group  Group	CC (aromatic bond)	CH (aromatic)	Aryl C-N (aniline)	Aryl C-N (nitro)	Aryl C-O	$NO_2$ group	$NH_2$ group	OH group

	HU	Group	0000	1.26430	00100	0.91800			0.971651				0.956	(phenol)		50030	0.0072	0.77615	0:120:5		
	TIL	WH ₂	Croup	1.24428		0.94134			70,000	0.99021			0.998	(aniline)			0.81370	0 77/60	0.75655		
[,	l		Group	1 33221	110001	1 15421	7.1.57.1	1.22157		1.22157			1.224	(nitromethane	,	, , , ,	0.66526		0.86639		
	erimental values	C-O (a)	Group	UCC07 1	1.00440	, 00000	1.29/00		1.37268					1.364	(loueud)		1 07126	1.0/1/20	0 77101	0.77101	
	mpounds and exp	C-N (b)	Group		1.97794		1 40639			1 10016	1.40040							1.39079		0.71104	
	of arry nitro CO	C-N (a)		dnord		1.81158		1.34595		1,42449		-		1.431 (aniline)			1 21254	1.212.1	0 74297		
	3040	I bond parameter	CH (1)	Croup	1,000	1.60061		1.03299			1.09327			* O	1.084	(bhenot)		2,000,	C0777.1	7537	0.04557
		The geometrica	ال الم	Group	1	1.47348		1.31468			1 30140	07176.1			1.397 avg.	(nhenol)			0.66540		0.89223
OH group  Table 15.250. The geometrical bond parameters of aryl nitro compounds and experimental values [1]. $C = N$ (a) $C = N$ (b) $C = O$ (a)			Parameter		0 (a)	(0.)	0, (0)	(on) 2	Bond	[ enoth	ייישנייין	2c'(A)	Evn Bond	I anoth	Lengui	(\vec{A})		2009	(0,) 2,0		

Bond	Atom														
		(e, ",	(eV)	(eV)	(eV)	Final Total Energy	Tailed ( )	, ( )	F _{con} (C2sp³)	$E(C2sp^3)$	.6	θ,	θ,	d,	d ₂
(20) 11 (20)		-	Bond 2	Bond 3	Bond 4	(25p) (eV)	(6)	(a)	Final	(eV) Final	€ 	<u> </u>	©	(°)	(4,)
(H) H-)	ئ	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.70507	17.00223	2,000,1					
$\left(C_{s} = \right)_{2} C_{s} O - H$	0	-0.74804	0	c	0		1 00000	0 6726	#5600.11-	-10.90248	74.42	105.58	38.84	1.24678	0.21379
" (" ~ OH	١	-0.24804	20020					Control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the control of the contro			115.79	64.21	64.82	0.53799	0.38009
, y, y, y, y, y, y, y, y, y, y, y, y, y,	•	- -	CCDC9'0-	-0.85035	0	-154,06442	0.91771	0.78762	-17.27448	-17.08362	100.00	80.00	46.39	1.16026	0.13674
$\begin{pmatrix} c_k = \\ c_k = \end{pmatrix}$	0	-0.74804	0	¢.	0		1.00000	0.87363	15.57379		106.51	73.49	51.43	1.04871	0.2820
$\left(C_{i}^{s}\right)_{2}^{s}C_{i}OH$	^ن ً	-0.74804	-0.85035	-0.85035	0	-154.06442	17716.0	0.78762	-17.27448	-17.08362	33	61 39	2000		678477
.)=.)H=,)												4	ررور	0.76870	0.54598
$C = (H_2 N) (C_n)^{3r}$	ن" : ——														
$=(H)C_{\star}$ $C_{\mu}OH$	ڻ ئ 	-0.83035	-0.85035	-0.56690	0	-153,88327	0.91771	0.79397	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0 65523
$\sum_{k=1}^{N} \frac{\lambda_k}{(k_j \zeta_{\mu})} C_k = C$	<i>ਹ</i> *					-							:		2000
$C_{\rho} = \int_{C_{\rho}} C_{\rho} N H - H$	*	-0.56690	0	e	0		20000	0							
W - 5 ( * )	;	+				1	1,2004	0.06.392	-15.39265		121,74	58.26	67.49	0.47634	0,46500
3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3	ر. - ا	-0.56690	-0.85035	-0.85035	0	-153.88328	1221670	0.79597	-17.09334	-16.90248	88.49	15.19	41.01	1.36696	0.02101
$\left\langle C_{s} = \right\rangle C_{s} - NH_{z}$	N	-0.56690	0	0	O		0.93084	0.88392	-15.39265		96.32	83.68	46.43	o Super	
$C = \int_{0}^{\infty} C_{k} - C_{n}H_{3}$	ئ"	-0.36690	0	0	0	-152,18259	12212	0.88307	2000 21		1		G. Carlotte	1.24639	0.09736
(=) (; -(; H,	١	0.56600	20000						CHRECE	8/107'01-	75.38	106.62	34.97	1.68807	0.25279
) ₂ N(O) = 0	;	+	-0.65U23	-0,85035	0	-153 88328	0.91771	0.79597	-17.09334	-16.90247	61.56	118,44	28.27	1.81430	0.37901
RN(O) = O	2   2	-0.92918	0	0	0	-	1.00000	0.86359	-15.75493		30 221				
C= C - NO	₹ ;	8167671-	-0.92918	-0.36229	0		0 93084	0.79816	-17.04640		132.36	47.64	62,44	0.54089	0.61333
), d, 1102	,*	-0.36229	-0.85035	-0.85035	O	-153.67867	0.91771	0.80561	-16.88873	-16.69786	72.49	167.51	33.55	1.64875	0.24736
$C = \int_{2}^{\infty} C_{n} - NO_{2}$	~	-0.92918	-0,92918	-0.36229	0		0.93084	0.79816	-17.04640		71.53	108 d7	90 65	1,000	
$=(O_2N)C_a=C$	ئ	-0,36229	-0.85035	-0,85035	0	-153.67867	0.91771	0 80561	-16.88873	28709.81	375			Szen.	H77070
										00/07/01	134.03	45.35	59.47	0.74854	0,56614

Table 15.251. The MO to HO intercept geometrical bond parameters of aryl nitro compounds.  $E_T$  is  $E_T(alom - alom, msp^3.AO)$ .

Sond

Table 15.252. The energy parameters (eV) of functional groups of aryl nitro compounds.

Parameters	C=C Group	CH (i) Group	C-N (a) Group	C-N (b) Group	C-O (a) Group	NO ₂ Group	NH ₂	<i>OH</i> Group
$f_1$	0.75	1			Group	Group	Group	Group
$n_i$	2	1	1	1	1	2	2	1
n ₂	0	0	0	0	0	0	0	0
n ₃	0	0	0	0	0	0	<del>                                     </del>	0
C ₁	0,5	0.75	0.5	0,5	0.5	0.5	0.75	0.75
<i>C</i> ₂	0.85252	1 .	1	1	1	1	0.93613	1
<i>c</i> ₁	1	1	1	1	1	1	0.75	0.75
C ₂	0.85252	0.91771	0.84665	0.91140	0.79329	0.85987	0.92171	1
<i>c</i> ₃	0	1	0	0	0	0	0	1
C ₄	3	1	2	2	2	4	1	1
$c_{S}$	0	1	0	0	0	0	2	1
C ₁₀	0.5	0.75	0.5	0.5	0.5	0.5	1.5	0.75
$C_{2o}$	0.85252	1	1	1	1	1	1	1
$V_{e}$ (eV)	-101.12679	-37.10024	-32.76465	-31.36351	-34.04658	-106.90919	-78.97795	-40.92709
$V_p$ (eV)	20.69825	13.17125	10.10870	9.67426	10.49024	23.57588	28.90735	14.81988
T (eV)	34.31559	11.58941	9.04312	7.92833	10.11966	40.12475	31.73641	16.18567
$V_m$ (eV)	-17.15779	-5.79470	-4.52156	-3.96416	-5.05983	-20.06238	-15.86820	-8.09284
E(лотно) (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	0	-14.53414	-13.6181
$\Delta E_{H_2\lambda IO}(AO/110) (eV)$	0	-1.13379	-1.13379	-0.72457	-1.49608	0	0	0
$E_T$ (лотно) (eV)	0	-13.50110	-13.50110	-13.91032	-13.13881	0	-14.53414	-13.6181
E(n, AOIHO) (eV)	0	0	0	0	. 0	0	-14.53414	0 -
$E_T(H_2\Lambda N)$ (eV)	-63.27075	-31.63539	-31.63549	-31.63540	-31.63532	-63.27093	-48.73654	-31.63247
$E_T(atom-atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-1.13379	-0.72457	-1.49608	-3.71673	0	0
$E_T(\lambda to)$ (eV)	-65.53833	-32.20226	-32.76916	-32.35994	-33.13145	-66.98746	-48.73660	-31.63537
$\omega \left(10^{15}  rad  /  s\right)$	49.7272	26.4826	11.9890	17.8228	13.3984	19.0113	68.9812	44.1776
$E_{K}$ (eV)	32.73133	17.43132	7.89138	11.73128	8.81907	12.51354	45.40465	29.07844
$\overline{E}_D$ (eV)	-0.35806	-0.26130	-0.18211	-0.21927	-0.19465	-0.23440	-0.42172	-0,33749
$\overline{E}_{Kvib}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.15498 [54]	0.10539 [45]	0.12808 [19]	0.19342 [45]	0,40929 [22]	0,46311 [17-18]
$\overline{E}_{ m osc}$ (eV)	-0.25982	-0.08364	-0.10462	-0.16658	-0.13061	-0.13769	-0.21708	-0.10594
$E_{mag}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.11441	0.14803	0.11441
$E_T(Group)$ $(eV)$	-49.54347	-32.28590	-32.87379	-32.52652	-33.26206	-67.26284	-49.17075	-31.74130
$E_{initial}(\epsilon_i$ лотно) (eV)	-14.63489	-14:63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-13.6181
$E_{initial}(c, AO/HO) (eV)$	0	-13.59844	0	0	0	0	-13.59844	-13.59844
$E_D(Group)$ $(eV)$	5.63881	3.90454	3.60401	3.25674	3.99228	8.72329	7.43973	4.41035

Table 15.253. The total bond e
-

						_			Т			1		-		1				1
					Exp. 6	.(9	(2)	120 [50-52]	(penzene)	120 [50-52] (benzene)	123.2 [54]	(nitromethane)	118.5 [54]	(nitrobenzene)	109.0	0.511	(aniline)			
Relative	īg.	0046	0,00070	70007	Cal 8	13		120 19		16.611		126.52		118.82	109.84		113.89		120.05	
		0.0	5 5 5	주) 	٩	P.,	<u> </u>									1				
Total Dand Energy	(eV)	65.217	72.424	72.476	}	_	(i)		_	120.19			_			1	_	1		
Calculated	Fuerey (eV)	65.18754	72.47476 72.47476 72.47476	72.47476		$E_{T}$	(eV)	10000	-1.85836			-1.44915		-1.65376		,	0		•	
t	L mrg	-	700	0		ۍ	,		0.79232			0.81549		0.81670	0.01771	0.51711	1.06823		00000.1	
						ű	•					_		_	1	cr.n	0.75		0.75	
HO	Group	0	-00	0		ť	<b>r</b>		<b>-</b>						}	-	-		_	
H	M12	dina	0		Ì	ت	5		-			<u> </u>				0.75	-	-	57.0	2
2	≥ .	5				,	Atom 2		0.79232			0.81549		0.85395 (Eq.	((5.114))	0.91771	-	1	0.84665	(15.152))
24.	ž,	dnou	7 5	-	$p^3AO$ ).	,	C2 Atom 1		0 79232			0.81549		0,77945		_	0.93613	(13.248))	0.84665	(Eq. (15.152))
	C-0 (a)	dnoub	0 (	0	$r_{\rm const} = r_{\rm const} = r_{\rm const} = r_{\rm const} = r_{\rm const} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} = r_{\rm cons} $	Atom 2	Hybridization Designation	(Table 15.3.A)	27	5		24		0				<b>=</b>		z
	C − N (b)	Group	- 2 -		s[1]. E _r is	-	E Contombio Atom 2		01.51	-17.17210		-16,68411	·*	-[3,61806		-14.82575		Ξ		-14.53414
	C-N (a)	1	<del>o</del> 0 –		experimental value		Atom I Hybridization Designation	(Table 15.3.A)		34		24		\$		<u>-</u>		z.		6
	0 10		v d d	4 4	pur spuno		Erectombre Atom I			-17.17218		-16,68411	ວ້	69557	maneti la	-14 82575		-14,53414		-15.95955
					oitro com		2c' Terpinal Moms	(a ₀ )		4.5585		4 1231		1	_	3,6515		3.1559		3,9833
(15.58).	×	<i>C=C</i>	& & &	; ve ve	re of and	is or my.	2c' Rond 2	<u>}</u>		2,62936		2 30043	Creary	1	250845	1 83616	a lucari	1.88268	1	1.88268
s given by		,			a wordingto	c paramete	2c' Bond 1	("")		2.62936		r change	5+9D5-7		2.81279	norms c	460607	1,88268		2,69190
walues hased on composition is given by (15.58).		Name	Nitrobenzene 2,4-dinitrophenol	2-nitroaniline 3-nitroaniline 4-nitroaniline	Land sand	54. The bond ang.	Atoms of Angle			ZCCC aromatic)	HOO7	(aromatic)	, VM, V		ZCNO		20,00	ZHNH		AC_NH
values hase.	Values data	Fomsula	C,H,NO; C,H,N,O;	CH, N, O, C, H, N, O, C, H, N, O, O, C, H, N, O, O, C, H, N, O, O, C, H, N, O, O, O, O, O, O, O, O, O, O, O, O, O,		Table 15.7	Alo					=	` 							

### BENZOIC ACID COMPOUNDS

Benzoic acid compounds have a hydrogen of an aryl group replaced by a carboxylic acid group corresponding to an C-C(O)-OH moiety that comprises C=O and OH functional groups that are the same as those of carboxylic acids given in the corresponding section. The single bond of aryl carbon to the carbonyl carbon atom, C-C(O), is also a functional group. This group is also equivalent to the same group of carboxylic acids except that  $\Delta E_{H_2MO} \left(AO/HO\right)$  in Eq. (15.42) and  $E_T \left(atom-atom,msp^3.AO\right)$  in Eq. (15.52) are both -1.29147~eV which is a linear combination of  $\frac{-1.13379~eV}{2}$ ,  $E_T \left(atom-atom,msp^3.AO\right)$  of the C-H group that the C-C(O) group replaces, and that of an independent  $C2sp^3$  HO, -0.72457~eV (Eq. (14.151)).

Examples include benzoic acid, chlorobenzoic acid, and aniline carboxylic acid with formulas  $C_7H_6O_2$ ,  $C_7H_5O_2Cl$ , and  $C_7H_7NO_2$ , respectively. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic 15 Compounds section. The  $NH_2$  and C-N functional groups of aniline carboxylic acids are the same as those of aniline given in the corresponding section. The C-Cl functional group of 2-chlorobenzoic acids corresponding to meta substitution is equivalent to that of chlorobenzene given in the corresponding section. The C-Cl functional group of 3 or 4-chlorobenzene, except that  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom, msp^3.AO)$  in Eq. (15.52) are both -0.92918~eV (Eq. (14.513)) since each of these positions can form a resonance structure with the carboxylic acid group which is permissive of greater charge donation from the  $C2sp^3$  HO.

The symbols of the functional groups of benzoic acid compounds are given in Table 15.255. The corresponding designations of benzoic acid is shown in Figure 64. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of benzoic acid compounds are given in Tables 15.256, 15.257, and 15.258, respectively. The total energy of each benzoic acid compound given in Table 15.259 was calculated as the sum over the integer multiple of

each  $E_D(Group)$  of Table 15.258 corresponding to functional-group composition of the molecule. The bond angle parameters of benzoic acid compounds determined using Eqs. (15.79-15.108) are given in Table 15.260.

5 Table 15.255. The symbols of functional groups of benzoic acid compounds.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH (i)
C-C(O)	C-C(O)
C=O (aryl carboxylic acid)	C = O
(O)C-O	C-O
OH group	OH
Cl-C ( $Cl$ to aromatic bond of 2-chlorobenzoic acid)	C-Cl (i)
Cl – C (Cl to aromatic bond of 3 or 4-chlorobenzoic acid)	C-Cl (ii)
Aryl C-N (aniline)	C-N
NH ₂ group	$NH_2$

		$\neg$	-т		7		$\neg$	-7
	NH2	Group 1 24478	0.04134	0.99627		0.998 (aniline)		0.81370
	C-N	Group 1.81158	1 34505	1.42449		1.431 (aniline)		1.21254
	C C! (ii)	2.19358	1.64243	1.73827		1.737 (chlorobenzene)	1 45.400	1.45403
	C-Cl (i)	2,20799	1.64782	1.74397		1.737 (chlorobenzene)	1 45057	1.40507
	HO Group	1,26430	0.91808	0.971651		0.972 (formic acid)	0.86025	0.0022
	C-O Group	1.73490	1.31716	1.39402		1.393 (methyl formate)	1 12915	0.75071
intal values [1].	C=0 Group	1,29907	1.13977	1.20628		1.214 (acetic acid)	0.62331	0.87737
compounds and experime	C-C(O) Group	1.95111	1.39682	1.47833		1.48 [55] (benzoic acid)	1.36225	0,71591
rameters of benzoic acid	CH (i) Group	1.60061	1.03299	1.09327		(benzene)	1.22265	0.64537
radic 13.230. The geometrical bond parameters of benzoic acid compounds and experimental values [1	C = C Group	1.47348	1.31468	1.39140		1.399 (benzene)	0.66540	0.89223
1 4015 13.430.	Parameter	a (a ₀ )	c. (a,)	Bond Length $2c'(\dot{A})$	Exp. Bond	Length $(A)$	$b,c(a_0)$	а

Table 15.257. The MO to HO intercept geometrical bond parameters of benzoic acid compounds. $E_r$ is $E_T(alom - alom, nxp^2/AO)$	netrical bong	i parameters of b	renzoic acid com	pounds. $E_r$ is .	$E_{\tau}(atom - atom)$	", msp. AO).									
Bond	Atom	Ε _τ (eV)	Ε _τ (eV)	E _T (eV)	E _T (eV)	Final Total Energy	$r_{noined}$ $(a_a)$	$(a_0)$	Energy (C2sp²) (eV) (eV)	$E(C2sp^2)$	. _е ©	ø ©	(c)	(a ₀ )	(a, l, l)
		Bond i	Bond 2	Bond 3	Bond 4	(eV)			min .	Final					
C-H (C,H)	نځ	-0,85035	-0.85035	-0.56690	0	-(53.88327	0.91771	0.79597	-17.09334	-16,90248	74.42	105.58	38.84	1,24678	0.21379
; ;; ;; ;; ;; ;; ;; ;; ;; ;; ;; ;; ;; ;;	ن			-											
('=(HOOC; )C, =C(H),	ຳ ບ້	55050	.0 85035	06995 0-	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0,75935	0.55533
$(C = (C) / C_n = C_k(H)$	ن ژ														
$C = (H_2N)C_r = C_b(H)$	;* 							1							
$\left(C_{b}\right)^{2}C_{a}(0)O-H$	O	-0.92918	Ø	0	0		000001	0.86359	-15.75493		115.09	64.91	64.12	0.55182	0.36625
$C_{r} = C_{r} = C_{r}(O) - OH$	С	-0.92918	0	0	0		000001	0.86359	-15,75493		101.32	78.68	48.58	1,14763	0.16950
$\begin{pmatrix} C_{r} = C_{r}(0) - OH \end{pmatrix}$	ر.	-0.92918	-1,34946	-0.64574	0	-154.54007	17716.0	0.76652	-17,75013	-17.55927	93.11	86.89	42.68	1,27551	0.04163
$\begin{pmatrix} C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_{\rho} & C_$	0	-1,34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0,52193	0.61784
$\begin{pmatrix} C_{b} & C_{b} \\ C_{b} & C_{b} \end{pmatrix} = O$	ڻ	-1.34946	-0.64574	-0.92918	0	-154.54007	17716.0	0.76652	-17.75013	-17.55927	134.03	45.97	62.14	0.60699	0.53278
$C_{\nu} = (HOOC_{\nu})C_{\nu} = C_{\nu}$ $(C_{\nu} = (HOOC_{\nu})C_{\nu} = C_{\nu}$ $(C_{\nu} \text{ bound to } H, C', \text{ or } NH,)$	ڻ	-0.64574	-0.85035	-0.85035	0	21296212	17716.0	0.79232	-17.17218	-16.98132	134.09	45.91	58.79	0.76344	0.55124
('=') ('-')	ū	-0.36229	0	0	0		1.05158	0.89582	15.18804		82.92	92.08	37.22	1.75824	0.11042
C = C = C	ບ້	-0.36229	-0.85035	-0.85035	c	-153.67867	17716.0	0.80561	-16,88873	-16.69786	73.32	106.68	31.67	1.87911	0.23129
$C_{r} = (C_{r})^{C_{r}} = C_{r}$ $C_{r} = (C_{r})^{C_{r}} = C_{r}$ $C_{r} = (C_{r})^{C_{r}} = C_{r}$ $C_{r} = (C_{r})^{C_{r}} = C_{r}$	ڻ	-0.36229	-0.85035	-0.85035	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	134.65	45,35	59.47	6.74854	0,56614
$\begin{pmatrix} c_r \\ C_r = \end{pmatrix} C_L NH - H$	N	06995-0-	0	o	0		0.93084	0.88392	-15.39265		121.74	58.26	67.49	0.47634	0.46500
$\left(\frac{s}{C_t}\right)_{C_s} = \frac{s}{C_s} - NH_2$	ره	-0,36690	-0.85035	-0.85035	0	-153.88328	17716.0	0.79597	-17.09334	-16.90248	88.49	15,16	41.01	9699€7	0.02101
$\left(C_{h}^{3}\right)C_{u}-NH_{2}$	×	06995-0-	С	0	0		0.93084	0.88392	-15.39265		96.32	83,68	46.43	1.24859	0.09736
C = (H,N)C = C	ڻ	-0.85035	-0.85035	-0.56690	0	-153.88327	17716.9	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0,75935	0.55533

Table 13.230. The energy parameters (c.v.) or university Eroups or	יז (בג) חו וחוומ	TOTAL ELOUDS OF	ะเ	inponins.						
Parameters	C=C Group	(.H (j) Group	C-C(0)	C=0 Group	Croup Group	OH Group	C C! (i) Group	C C/ (ii) Group	C-N Group	Oroup
1	0.75	-								
1	2	-	_	2	_	-	1	1	-	7
n,	0	0	0	0	0	0	0	0	0	0
n,	0	0	0	0	0	٥	٥	0	0	-
	0.5	0.75	0.5	0.5	0.5	0.75	0.5	0.5	0.5	0.75
	0.85252	-	-	-	-	_	0.81317	0.81317	1	0.93613
	-		_	-	-	0.75	-	1	1	0.75
	0.85252	0.91771	0.91771	0.85395	0.85395	-	_	_	0.84665	0.92171
* 6	C	-	0	2	0	_	0	0	0	0
	m	-	2	4	2	-	2	2	2	-
	0	_	0	0	0	-	0	0	0	2
	0.5	0.75	5.0	0.5	0.5	0.75	0.5	0.5	0.5	1.5
	0.85252	_	-	-		1	0.81317	0.81317	1	-
V, (eV)	-101.12679	-37.10024	-32.15216	-111.25473	-35.08488	-40.92709	-31.85648	-32,14474	-32.76465	-78.97795
V, (eV)	20.69825	13,17125	9.74055	23.87467	10.32968	14.81988	8,25686	8.28394	10.10870	28.90735
T (eV)	34,31559	11,58941	8.23945	42.82081	10,11150	16,18567	7.21391	7.32700	9,04312	31.73641
(eV)	-17.15779	-5.79470	4.11973	-21,41040	-5.05575	-8.09284	-3.60695	-3.66350	-4.52156	-15,86820
E(n 10) (cV)	0	-14.63489	-14.63489	0	-14.63489	-13.6181	-14.63489	-14.63489	-14.63489	-14.53414
ΔE _{n, vo} (so no) (eV)	0	-1,13379	-1.29147	-2.69893	-2.69893	0	-2.99216	-2.99216	-1.13379	0
E. (40 110) (eV)	0	-13,50110	-13,34342	2.69893	-11.93596	-13.6181	-11.64273	-11.64273	-13.50110	-14.53414
E(4, 10 10) (eV)	0	0	0	0	0	0	0	0	0	-14.53414
E. [11,210] (cV)	-63.27075	-31,63539	-31.63530	-63.27074	-31,63541	-31.63247	-31,63539	-31.63542	-31.63549	-48.73654
$E_{\tau}(atom - atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-1.29147	-2.69893	-1,85836	0	-0.72457	-0.92918	-1.13379	0
$E_{r_{r_{r_{1}}}(sm)}(eV)$	-65,53833	-32.20226	-32.92684	-65.96966	-33.49373	-31.63537	-32.35994	-32.56455	-32.76916	-48.73660
ω (1012 rad / s)	49.7272	26.4826	10.7262	59.4034	24,3637	44.1776	8.03459	8.11389	11.9890	68.9812
$E_r$ (eV)	32,73133	17.43132	7.06019	39.10034	16,03660	29.07844	5.28851	5.34070	7.89138	45,40465
Ē, (eV)	-0.35806	-0.26130	-0.17309	-0.40804	-0.26535	-0.33749	-0.14722	-0.14888	-0.18211	-0.42172
E kon (eV)	0.19649	0.35532 Eq. (13.458)	0.10502	0.21077	0,14010	0.46311	0.08059 [12]	0.08059 [12]	0.15498 [54]	0.40929
E (eV)	-0.25982	-0.08364	-0.12058	-0.30266	-0.19530	-0.10594	-0.10693	-0.10859	-0.10462	-0.21708
E (eV)	0.14803	0.14803	0.14803	0,11441	0.14803	0.11441	0.14803	0.14803	0,14803	0.14803
Er (Guy) (eV)	-49.54347	-32,28590	-33.04742	-66.57498	-33,68903	-31.74130	-32.46687	-32.67314	-32.87379	-49.17075
E (c. 10 110) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-13.6181	-14.63489	-14.63489	-14,63489	-14,53414
Emple, so no) (eV)	0	-13,59844	0	0	0	-13,59844	0	0	0	-13.59844
$E_{p}(\alpha_{mp})(eV)$	5.63881	3.90454	3.77764	7.80660	4,41925	4.41035	3.19709	3.40336	3.60401	7.43973

							to the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the same of the	O Johnson of	Toble 15.7	X COUNTRY	to the expens				ì			
Table 15.259. The total bond energies of benzoic acid compounds calculated using the hundronal troup composition and are energies of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the properties of the	al bond energies	of benzoic	acid comp	ounds calcula	ted using the fund	tronal group	composition and the	G Gliciping	C-C/ (i)	9 (9)	C-C! (ii)	χ~5	NH2	Calculated Total Bond		Experimental Total Bond Energy	Relative	
Commits	Name	ر ر:: ر::		C# 3	(2) - 1	ر ا ا	C Indian	Group	Group		Group	Group	Group	Energy (eV)		(e)	- }	
Commen		Group	}	dno	Oroup	danin		-	0		0	0	۵	73.769		73,762	-0.UNRUS	
	icid	٠ ټ		י מי		- c			_		0	0 1	20	190.61		73.261		
٠,	2-chlorobenzoic acid	= `				-	-		-			<b>&gt;</b> 0	> <	73 26		75.247		
	3-chlorobenzoic acid	6 4		, -4		_		_	5		- 0	> ~	-	80.90		80,941		
	4-chlarobenzate acid	2 40		3			1				- c		•	80,90857		80,813	-0.00118	
C,H,NO. Andino-3	Antine-2-carboxyle acid	<b></b>		77							0	-	-	80,90	1	80.949	1	
South							,	, ,										
Table [5,260. The bond angle parameters of benzoic acid compounds and experimental values [1]. E. 18 E. (alian - dout, hisp. Art.)	nd angle paramet	ers of benz	oic acid co	mpounds an	i experimental va	lues [1]. £,	is E _T (afom – afoil	I, msp Acc)			-	-	1	4	-	1	Exp. θ	Γ
Moms of Angle	20.	2r'	2c' Terminal	E-Continuentes	Alom 1 Hybridization	F. Contoning	Atom 2 Hybridization	C ₂	C ₂	 ن	 ن"	ซ" 	(eV)	o' ©	, <u> </u>	© "©	(E)	
	(°)	(0")		- Victoria	Designation		Designation									-		T
	-		(0,1)		(Table 15.3.A)		(Table 13.5.A)	0 70033	0.707.0	-	-	1 0.79232	-1.85836			120.19	(benzene)	
(aromatic)	2.62936	2,62936	4.5585	-17,17218	其	17.17218	#	0.19432	1000		-	-	-		120.19	119.91	120 50-52	Γ
H.J.)77	-										-	-	$\downarrow$	+	+	10,000	(Denzere)	T
(aromatic)	-	73,768	3,6,105	11.89575	-	.14 82575	-	~	0.91771	0.73	-	17710.0 57.0	1 0	1	1	107.71		T
Zi.0,H	(chs97	1.63000	Popular C				,	0,79232	0.85395	-		0.82313	3 -1.65376			121.86	122 [55]   (benzoic acid)	
0".5".57	2.82796	2.27954	4,4721	-17.17218	<del>,</del>	-13.61806	<b>)</b>		(15.114))	-	-		4	+	+	+	125,011	T
	Yarran C	1969	7 6700	16 40067	2	-13,61806	0	0.82959	0.85395 (Eq.			1 0.84177	7 -1.65376			117,45	(benzoic acid)	7
Z( ), ), ),	061787			1677191		-(5,75493	,		(15,114))	-	-	1 0.85237	7 -1,44915		-	126.03	122 [55] (berzois acid)	
*0"0"07	2,17954	2 63431	4.3818	ο,	7.	o,	7	C114%D	U.MB329	-	+		1		+	+	120	T
		_															(ZCC(H)C	
																	121.7	
71.1.2	95029 (	2,62936	4.5585	-17,17218	æ	17,17218	æ	0.79232	0.79232	_		0.79252	12 -1.85836			150.15	(יככ(נו)ט	
(aromatic)																	chlorobenzene) 120 [58-52] thenzene)	~
			_							+	+	+				-	120 (50-32)	
H.J.)7															120,19	16.611	(benzene)	
(aromatic)		1						0,93613			-	20000	5			113.89	113.9	
HNH7	1,88268	1,88268	3.1559	-14.53414	z	Œ	æ	Eq. (13,248))		-	-	0,75	-	-		+	_	
W. WH	2,69190	1.89268	3,9%35	-15.95955	t	+14:53:41+	z	0.84665 (Eq.	0.84665 (Eq.	67.0	-	0.75 1.00000	0 00			120.05		

# ANISOLE

Anisole has the formula  $C_7H_8O$  and comprises the phenol molecule with the hydroxyl hydrogen atom replaced by the moiety  $-O-CH_3$  to form an ether comprising aromatic and methyl functional groups as well as two types of C-O functional groups, one 5 for aryl carbon to oxygen and one for methyl carbon to oxygen. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The  $CH_3$  and methyl C-O functional groups are the same as those of the corresponding ether groups given in the corresponding section.

The C-O functional group comprising the bond between the ether oxygen and aromatic ring is equivalent to that of the methyl ether C-O functional group except that  $\Delta E_{H_2MO} \left(AO/HO\right)$  in Eq. (15.42) and  $E_T \left(atom-atom,msp^3.AO\right)$  in Eq. (15.52) are both -1.13379~eV (Eq. (14.247)).  $E_T \left(atom-atom,msp^3.AO\right)$  is based on the energy match between the  $OCH_3$  group and the  $C2sp^3$  HO of the aryl group and is twice that of the aryl C-H group that it replaces.

The symbols of the functional groups of anisole are given in Table 15.261. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of anisole are given in Tables 15.262, 15.263, and 15.264, respectively. The total energy of anisole given in Table 15.265 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.264 corresponding to functional-group composition of the molecule. The bond angle parameters of anisole determined using Eqs. (15.79-15.108) are given in Table 15.266.

Table 15.261. The symbols of functional groups of anisole.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH (i)
Aryl C-O	C-O (a)
Methyl C-O	C-O (b)
CH₃ group	$C-H$ $(CH_3)$

	$C-H(CH_3)$	Group	1,64920	1.04856	1.10974	111/2	(toluene)	1,27295	0.63580
mental values [1].	C-0 (b)	Group	1.80717	1.34431	1.42276			1,20776	0 74388
Table 15.262. The geometrical bond parameters of anisole and experimental values [1]	(O (a)	Group	1.82682	1,35160	1.43047			1.22900	0 73986
d parameters of a	(.) H.)	Group	1,60061	1.03299	1.09327	1 004	(phenol)	1.22265	0.64537
he geometrical bo	C=C	Group	1.47348	1.31468	1.39140	1 307 0101	(phenol)	0.66540	0.89223
Table 15.262, 7	Parameter		a (a _a )	c' (a ₀ )	Bond Length $2c'$ $(\vec{A})$	Exp. Bond	(A)	$b,c$ $(a_a)$	В

table 15,203. The MO to HO intercept geon	netricai bon	d parameters of	antsole. $L_T$ is	$e_{r}$ (atom – atom, msp	msp'.AO).	
Bond	Atom	E.	E.	-3	E.	Final Total

Bond	Atom	E	E ₇	E,	E	Final Total	f	7	$E_{c,t,s,s}(C2sp^3)$	E(C)sn3	θ.	9	6	P	P
		(eV) Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C2sp³ (eV)	(a _o )	(a _n )	(eV) Final	(eV) Final	(0)	T ©	. O	(a°)	(a ₀ )
$C - H\left(C_{x}H\right)$	۲,	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17,09334	-16.90248	74,42	105.58	38.84	1.24678	0,21379
$C - H \left( OC_e H_3 \right)$	ڻ	-0.72457	0	0	0	-152,34026	0.91771	0.87495	-15.55033	-15.35946	78.85	101.15	42.40	171171	0.16921
$\left(C_{b}\right)_{2}^{2}C_{a}O-C_{a}H_{3}$	ڻ	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15,55033	-15.35946	95.98	84,02	46.10	1,25319	0.69112
$\left(C_{s}\right)_{2}^{2c}C_{s}O-C_{s}H_{3}$	0	-0.72457	-0.56690	0	0		1.00000	0.84418	-16.11722		93.38	86.62	44.25	1.29456	0 04975
$\left(C_{b} = \sum_{1}^{3c} C_{u} - OC_{r}H_{3}\right)$	ڻ	-0.56690	-0.85035	-0.85035	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	87.00	93.00	40.30	1.39329	0.04170
$\left(C_{b} = \sum_{i}^{A_{c}} C_{i} - OC_{c}H_{3}\right)$	0	-0.56690	-0.72457	0	0		1.00000	0.84418	-16.11722		91.59	88.41	43.36	1.32814	0.02346
$\left(C_{\mu}\right)_{2}^{3}C_{\mu}OC_{\mu}H_{3}$	نَ	-0.56690	-0.85035	-0.85035	C	-153.8K327	17716,0	0.79597	-17.09334	-16.90248	134,24	45.76	38.98	0.75935	0.55533
$\begin{pmatrix} x' \\ = (H)C_* \end{pmatrix} C_* O C_* H_3$	ij	-0,85035	-0,85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Parameters $C = C \cap CH \cap CH \cap CH \cap CH \cap CH \cap CH \cap CH$	ر پی _ا ر	(I)	C-O (a)	(q) O-3	$CH_3$
$f_{\rm t}$	Srout Group	Group	Group	Group	Group
	0.75	-			
lu!	2		1	_	3
72	0	0	0	0	2
n,	0	0	0	0	0
び	0.5	0.75	0.5	0.5	0.75
<i>C</i> ₂	0.85252	1	1	1	-
c.	_	-	1	1	1
5	0.85252	0.91771	0.85395	0.85395	0.91771
ູ້	0	-	0	0	0
2	3	1	2	2	-
ో	0	-	0	0	3
Ü	0.5	0.75	0.5	0.5	0.75
, C.	0.85252	1	1	1	-
V, (eV)	-101.12679	-37.10024	-32.67197	-33.1 <i>5757</i>	-107.32728
V, (eV)	20.69825	13.17125	10.06645	10.12103	38.92728
T (eV)	34.31559	11.58941	8.94231	9.17389	32,53914
V (eV)	-17.15779	-5.79470	-4.47115	-4.58695	-16.26957
E(somo) (eV)	0	-14.63489	-14.63489	-14.63489	-15.56407
$\Delta E_{H_2MO}$ (sound) (eV)	0	-1.13379	-1.13379	-1.44915	0
$E_{\tau}(sano)$ (eV)	0	-13.50110	-13.50110	-13.18574	-15.56407
$E_T(u_2 w)$ (eV)	-63.27075	-31.63539	-31.63547	-31.63533	-67.69451
$E_T(atom - atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-1.13379	-1.44915	0
$E_{\tau}(s\nu) (eV)$	-65.53833	-32,20226	-32.76916	-33.08452	-67.69450
$a (10^{15} rad/s)$	49.7272	26.4826	11.8393	12.0329	24.9286
$E_{K}$ (eV)	32.73133	17.43132	7.79284	7.92028	16.40846
$\vec{E}_{D}$ (eV)	-0.35806	-0.26130	-0.18097	-0.18420	-0.25352
$\overline{\overline{E}}_{Krb}$ $(eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.13663	0.13663 [21]	0.35532 (Eq.
Ē., (eV)	-0.25982	-0.08364	-0.11266	-0.11589	-0.22757
$E_{nig}(eV)$	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\mathrm{T}}(inup)$ (eV)	-49.54347	-32,28590	-32.88182	-33.20040	-67.92207
$E_{utind}(\epsilon_1, \kappa_{IIIO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Euthal (4, 101110) (eV)	0	-13.59844	0	0	-13.59844
$E_D$ (cimup) (eV)	5.63881	3.90454	3.61204	3.93062	12.49186

Table 15.265. The total bond energies of anisole calculated using the functional group composition and the energies of Table 15.264 compared to the experimental Role Formula Name $C = C \ CH \ (i) \ C = O \ (i) \ C = O \ (b) \ CH \ (i) \ C = O \ (i) \ C = O \ (ii) \ C = O \ (iii) \ C = O \ (iii) \ C = O \ (iiii) \ C = O \ (iiii) \ C = O \ (iiii) \ C = O \ (iiiii) \ C = O \ (iiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiii$	values	five
. 15.265. The total bond energies of anisole calculated using the functional group composition and the energies of Table 15.264 compa Name $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C = C$ ( $H$ ) $C$ ( $H$ ) $C$ ( $H$ ) $C$ ( $H$ ) $C$ ( $H$ ) $C$ ( $H$ ) $C$ ( $H$ ) $C$ ( $H$ ) $C$	imental	Relative
15.265. The total bond energies of anisole calculated using the finetional group composition and the energies of T Name $C = C  (H  (i)  C = O  (b)  (C = O  (b)  CH_s$	impared to the experi	Experimental Total Bond Energy
15.265. The total bond energies of anisole calculated using the functional group composition and the Name $C=C$ (a) $C=C$ (b) $C=C$ (c) $C=C$ (c) $C=C$ (d) $C=C$ (d) $C=C$ (e) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f) $C=C$ (f)	of Table 15.264 co	Calculated Total Bond
15.265. The total bond energies of anisole calculated using the functional group. Name $C=C$ (3) (3) Group	and the energies	CH,
15.265. The total bond energies of anisole calculated using the Name $C = C$ (H (i)	oup composition	(7-0 (b) Group
15.265. The total bond energies	g the functional gr	(' ~ () (a) Group
15.265. The total bond energies	calculated usin	(J) H.J
15.265. The	ties of anisole	C=C
Table 15. Formula	265. The total bond energ	Namo
	Table 15.	Formula

	E		1021	(ben	120 [3
	(°)		120 19		1001
	6,0				
	θ ⁻ (0)				120 10
	, (°)				
	E ₇ (eV)		-1.85836		
	٧.		0.79232		
	<i>5</i> -		-		
	5		-		
	ڻ		-		
	C ₂ Aton 2		0.79232		
	C ₂ Aton I		0.79232 0.79232		
m,msp*.AO).	Atom 2 Hybridization Designation (Table 15.3.4)		ह		
$_{T}(atom-ato$	Erosbenbe Atım 2		-17.17218		
perimental values [1]. $E_T$ is $E_T(alom - alom, msp^2.AO)$	Atom   Hybridization Designation (Table 15.3.A)	;	34		
perimental v	Erailundic Atom I	10010	-1/.1/218		
ie and ex	2c' Terminal Atomis (a ₀ )	1022	4.3363	_	
o alino	2c' Bond 2 (a ₀ )	2000	4.02230		
c parameter	2c' Bred 1 (a _o )	250526	DCC20.7		
and a supplied and experimental of an and experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimental of an experimen	Atoms of Angle	ZCCC	(aromatic)	ZCCH	(aromatic)

## **PYRROLE**

Pyrrole having the formula  $C_4H_5N$  comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to a NH functional group. The two symmetrical carbon-to-nitrogen bonds comprise the C-N-C functional group. The 1,3-5 but diene moiety comprises C-C, C=C, and CH functional groups. The C-C and C = C groups are equivalent to the corresponding groups of 1,3-butdiene given in the Cyclic and Conjugated Alkenes section except that the energies terms of the corresponding to oscillation in the transition state match pyrrole. Furthermore, the conjugated double bonds have the same bonding as in 1,3-but diene except that the hybridization terms  $c_2$  of the C-C10 and C=C groups and  $C_2$  and  $C_{2o}$  of the C=C group in Eqs. (15.42) and (15.52) become that of benzene given bу Eq. (15.143), $(C_2(benzeneC2sp^3HO) = c_2(benzeneC2sp^3HO) = 0.85252)$ , in the cyclic pyrrole MO which has aromatic character. The bonding in pyrrole, furan, and thiophene are the same except for the energy match to the corresponding heteroatoms. The hybridization permits double-bond 15 character in the carbon-heteroatom bonding.

The NH group is solved equivalently to that of a secondary amine as given in the corresponding section except that the hybridization term  $c_2$  is that of the amino group of aniline in order provide double-bond character to match the group to the other orbitals of the molecule. Similarly, the CH functional group is equivalent to that of 1,3-butdiene, except that  $\Delta E_{H_2MO} \left(AO/HO\right) = -2.26758 \, eV$  (Eq. (14.247)) in Eq. (15.42) in order to provide matching double-bond character.

The solution of the C-N-C functional group comprises the hybridization of the 2s and 2p AOs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the C-N-C-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52). The hybridization factor  $c_2(arylC2sp^3HO\ to\ N) = 0.84665$  (Eq. (15.152)) matches the double-bond character of the  $C2sp^3$  HOs to the N atom of the NH group, and  $C_2$  and  $C_{2o}$  in Eqs. (15.42) and (15.52)

become that of benzene given by Eq. (15.143),  $C_2$  (benzeneC2sp³HO) = 0.85252. Furthermore,  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp³.AO)$  in Eq. (15.52) are both -0.92918 eV (Eq. (14.513)) per atom corresponding to -3.71673 eV in total. This is the maximum energy for a single bond and corresponds to methylene character as given in the Continuous-Chain Alkanes section.

The symbols of the functional groups of pyrrole are given in Table 15.267. The structure of pyrrole is shown in Figure 65. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of pyrrole are given in Tables 15.268, 15.269, and 15.270, respectively. The total energy of pyrrole given in Table 15.271 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.270 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrrole determined using Eqs. (15.79-15.108) are given in Table 15.272.

15 Table 15.267. The symbols of functional groups of pyrrole.

Functional Group	Group Symbol
$C_a = C_b$ double bond	C = C
$C_b - C_b$	C-C
$C_a - N - C_a$	C-N-C
NH group	NH
CH	CH

	CH	Group	1.53380	1.01120	1.07021	1.076 (pyuole)	1.15326	00000
	NH	Group	1.24428	0.94134	0.996270	0.996 (pyrrole)	0.81370	(3732.0
rimental values [1].	C-N-C	Group	1.43222	1.29614	1.37178	1.370 (pyrrole)	0.60931	0 00400
Table 15.268. The geometrical bond parameters of pyrrole and experimental values [1],	2-2	Group	1.77965	1,33404	1.41188	1.417 (pyrrole)	1.17792	0.74961
s geometrical bond paran	2=2	Group	1.45103	1.30463	1.38076	1.382 (pyrrole)	0.63517	0.89910
Table 15.268. The	Parameter		a (a ₀ )	$c'(a_0)$	Bond Length $2c'(A)$	Exp. Bond Length $(A)$	$b,c$ $(a_0)$	0

and any strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the strength of the streng		to constitution of	Pyrion. 1, 10 a	iii aingi Broup an	ייי אייי שוב	11 OF AIRYFEIO	ups. 27 15 27	, arom - arom,	msp .AU ).						
Bond	Аюл	# # # # # # # # # # # # # # # # # # #	E ₇ (eV) Bond 2	#. (eV) Bond 3	E ₇ (eV) Bond 4	Final Total Energy (72sp³ (eV)	$\binom{r}{a_o}$	$(a_0)$	$E_{coron}(C2xp^3)$ (eV) Final	$E((72xp^3)$ (eV) Final	(e)	(o)	(°)	(a ₀ )	(a _o )
('-H ((',H)	'ر	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	83.33	96,65	43.94	1.10452	0.09331
C-H (C,H)	ڻ"	-1.13380	-1.13380	0	0	-153.88328	1//16.0	0.79597	-17.09334	-16.90248	82.21	97.79	43.14	1,11914	0.10794
$C_{\mu} = (H)C_{\mu} - C_{\mu}(H) = C_{\mu}$	υ,	-1.13380	-1.13380	0	0	-153,88328	12216'0	0,79597	-17.09334	-16.90248	75.19	88.43	42.49	131226	0.02177
$C_a = C_b(H)(H)C_b = C_a$	ů,	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17,09334	-16.90248	136.36	43.64	59.86	0.72857	0.57606
	· t	-1.[3380	-0.92918	-	0	-153.67867	17716.0	0.80561	-16.88873	-16.69786	136.75	43.25	60.35	0.71784	0.58678
$C_{\alpha}(H)N - C_{\alpha} = C_{\beta}(H)$	¿³	-1.13380	-0.92918	0	0	-153.67867	17716.0	0.80561	-16.88873	-16.69786	138.54	41,46	60,13	0.69238	0,60376
$C_{\mu}(H)N-C_{\mu}=C_{\mu}(H)$	×	-0.92918	-0.92918	0	С		0.93084	0.81549	-16.68411		I38.92	41.08	65.19	0.68147	0.61467
N-H(NH)	>	-0.92918	-0.92918	0			0.93084	0.81549	-16,68411		117.34	62.66	62.90	0.56678	0.37456

Table 15.269. The MO to HO intercept geometrical bond parameters of pyrrole. R is an alkyl group and  $R_{c}R_{c}^{*}R^{*}$  are H or alkyl

Table 15.270. The energy parameters (eV) of functional groups of pyrrole.

Parameters	C = C Group	C-C Group	C-N-C Group	<i>NH</i> Group	<i>CH</i> Group
n ₁ /	2	1	2	1	1
$n_2$	0	0	0	0	0
$n_3$	0	0	0	0	0
$C_1$	0.5	0.5	0.5	0.75	0.75
$C_2$	0.85252	1	0.85252	0.93613	1
<i>c</i> ₁	1	1	1	0.75	1
$c_2$	0.85252	0.85252	0.84665	0.92171	0.91771
<i>c</i> ₃	0	0	0	1	1
<i>c</i> ₄	4	2	4	1	1
$c_{5}$	0	0	0	1	1
$C_{lo}$	0.5	0.5	0.5	0.75	0.75
C ₂₀	0.85252	1	0.85252	1	1
$V_{e}(eV)$	-104.37986	-33.80733	-106.58684	-39.48897	-39.09538
$V_{p}(eV)$	20.85777	10.19898	20.99432	14.45367	13.45505
T(eV)	35.96751	9.49831	37.21047	15.86820	12.74462
$V_m(eV)$	-17.98376	-4.74915	-18.60523	-7.93410	-6.37231
Е(логно) (eV)	0	-14.63489	0	-14.53414	-14.63489
$\Delta E_{H_{2}MO}$ (AOIHO) (eV)	-2.26759	-1.85836	-3.71673	0	-2.26758
$E_{T}(AOIHO)$ (eV)	2.26759	-12.77653	3.71673	-14.53414	-12.36731
$E_T(H_2MO)$ (eV)	-63.27075	-31.63572	-63.27056	-31.63534	-31.63533
$E_T(atom-atom, msp^3.AO)$ (eV)	-2.26759	-2.26759	-3.71673	0	0
$E_{T}(MO)$ (eV)	-65.53833	-33.90295	-66.98746	-31.63537	-31.63537
$\omega \left(10^{15} \ rad \ / \ s\right)$	15.4421	12.3131	15.7474	48.7771	28.9084
$E_{\kappa}$ (eV)	10.16428	8.10471	10.36521	32.10594	19.02803
$\overline{\widehat{E}}_D$ (eV)	-0.20668	-0.19095	-0.21333	-0.35462	-0.27301
$\overline{E}_{Kvib}$ (eV)	0.17897 [6]	0.14829 [48]	0.11159 [12]	0.40696 [24]	0.39427 [56]
$\overline{E}_{osc}$ (eV)	-0.11720	-0.11680	-0.15754	-0.15115	-0.07587
$E_{mag}(eV)$	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{r}(Group)$ (eV)	-65.77272	-34.01976	-67.30254	-31.78651	-31.71124
$E_{initial}(c_{i} AOIHO) (eV)$	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489
$E_{initial}(c, AOIHO) (eV)$	0	0	0	-13.59844	-13.59844
$E_{p}(Group)$ (eV)	7.23317	4.74998	8.76298	3.51208	3.32988

Exp. θ (°)	121.5 (pyrrole)			127.1 (nymole)	,		1,721	107.7 (pyrrole)	8.601	107,4
(°)	120.51	131.97	120,37	127.20	130.36	125.76	127.23	107.52	109.83	10701
(e)		107.52					107.01			
9 (0)		12051					125.76			
φ, ©		_								
$E_{T}$ (eV)	0		0	0	0	0		-1.44915	-1.85836	-1.85836
'ধ'	1.00435		0.97435	1.05822	1.05822	1,03725		0.82131	0,76360	0.75927
ช	0.75		57:0	6.75	0.75	67.0		-	-	-
5	-		-	-	-	-		-	-	_
5	6,75		27.0	0.75	0.75	0.75		-	-	_
C ₂ ∧lom 2	0.92171 Eq. (15.151))		0.82493 (Eq. (15.64))	0.85252	0.85252	0.82562		0.79597	0.76360	0.75493
C2 Atom 1	0.91771		0.84665 (Eq. (15.152))	0.80561	0.80561	0.79597		0.84665 (Eq. (15.152))	0.76360	0,76360
Atom 2 Hybridization Designation (Table 15.3.B)	z		y	VS.	9	11		81	26	29
Erantoneks Alom 2	-14,53414		-16,49325	-15.95954 C,	-15.95954 C ₆	-16.47951 C _a		-17.09334 C,	16218711-	-18,02252
Atom I Hybridization Designation (Table 15.3.B)	-		z	51	15	81		z	26	38
L'Coeloube Mon I	-14 82575		-14,53414	-16.88873 C.	-16.88873 (',	-17.09334 C _b		-[4,534[4	-17.81791	19718.71-
Zc' Teminal Atoms (a ₀ )	4.0166		3,8987	4.2111	4.2111	4.1312		4.1952	4.2426	42426
2c' Hond 2 (a _p )	2.59228		2.59228	2 66807	2.60925	2.60925		2.60925	2.59228	2.66807
2c' Bond 1 (a _b )	2,02241		1.88268	2.02241	2.02241	2.02241		2.59228	2,59228	2,60925
A THE LANGUAGE	ZHC."N	ZC,C,H,	ZHNC."	7H,C,C,	ZH,C,C,	",)',)'H7	Z(',C',H',	ZNC,C,	"כנ"אנכ"	, , , , , , , , , , , , , , , , , , ,

### **FURAN**

Furan having the formula  $C_4H_4O$  comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the C-O-C functional group. The 1,3-butdiene moiety 5 comprises C-C, C=C, and CH functional groups. The CH, C-C, and C=C groups are equivalent to the corresponding groups of pyrrole given in the corresponding section.

The C-O-C functional group of furan is solved in a similar manner as that of the C-N-C group of pyrrole. The solution of the C-O-C functional group comprises the hybridization of the 2s and 2p AOs of each C to form a single  $2sp^3$  shell as an energy 10 minimum, and the sharing of electrons between two  $C2sp^3$  HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the C-O-C-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52). The hybridization factor  $c_2(arylC2sp^3HO\ to\ O) = 0.79329$  (Eq. (15.150)) matches the double-15 bond character of the  $C2sp^3$  HOs to the O atom, and  $C_2$  and  $C_{2o}$  in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143),  $C_2(benzeneC2sp^3HO) = 0.85252$ . Furthermore,  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) is  $-0.92918\ eV$  (Eq. (14.513)) per atom corresponding to  $-3.71673\ eV$  in total.

The symbols of the functional groups of furan are given in Table 15.273. The structure of furan is shown in Figure 66. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of furan are given in Tables 15.274, 15.275, and 15.276, respectively. The total energy of furan given in Table 15.277 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.276 corresponding to functional-group composition of the molecule.

The bond angle parameters of furan determined using Eqs. (15.79-15.108) are given in Table 15.278.

Table 15.273. The symbols of functional groups of furan.	ups of furan.
Functional Group	Group Symbol
$C_n = C_n$ , double bond	2=2
C', - C',	.))
C, -0-C,	J-0-C
CH	H.)

	_		_		,	Т		_
	H	Group	1.53380	1.01120	1.07021	1.075 (furan)	1.15326	0.65928
nental values [1].	J-0-J	Group	1.41546	1.28854	1.36373	1.362 (furan)	0.58583	0.91033
eters of furan and experir	.JJ	Group	1.77965	1.33404	1.41188	1,431 (firan)	1.17792	0.74961
Table 15.274. The geometrical bond parameters of furan and experimental values [1].	2=2	Group	1,45103	1.30463	1.38076	1.361 (furan)	0.63517	01668'0
Table 15,274. The	Parameter		$a(a_a)$	$c$ , $(a_0)$	Bond Length $2c'(A)$	Exp. Bond Length (A)	$h_i c \left( a_n \right)$	e

Table 15.275. The MO to HO intercept geometrical bond parameters of furan.  $R_i$  is an allyl group and  $R_iR_iR^n$  are H or alkyl groups.  $E_t$  is  $E_t(an)$ 

				The state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the s		TOP: delimina _ months et at se francia from to the title to the	1 1 1 1 1 1 1	Continuous I was							
Bond	Atom	(eV) Bond I	E _T (eV) Bond 2	E _T (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy C2xp³ (eV)	$\binom{r_{mind}}{(a_0)}$	, freed (a,)	$E_{color}$ (C2 $p^3$ ) (eV) Final	$E(C2sp^3)$ (eV) Final	(°)	(°)	(°)	(a ₀ )	$\begin{pmatrix} d_2 \\ (a_0) \end{pmatrix}$
('-H (C,H)	ບ້	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	83.35	96.65	43.94	1.10452	0.09331
$C-H(C_sH)$	ر. ۲	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	82.21	97.79	43.14	1.11914	0 10794
$C_{\mu} = (H)C_{\mu} - C_{\mu}(H) = C_{\mu}$	ڻ	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	91.57	88 43	42.40	131226	271000
$C_{\alpha} = C_{\lambda}(H)(H)C_{\delta} = C_{\alpha}$	نځ	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	136.36	43.64	98 65	0.77857	0.57606
$O(C_n = C_n/H)$	ن,	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	136.75	43.25	50.35	0.71784	20075.0
$C_aO - C_a = C_b(H)$	ن	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	140.16	39.84	61.75	0 66997	6700000
CO-C =C(H)	3	.0 97918	0.00019	c			00000	0,000						20000	701700

Table 15.276. The energy parameters (eV) of functional groups of furan.

Parameters	C = C Group	C – C Group	C-O-C Group	<i>CH</i> Group
$n_1$	2	1	2	1
$n_2$	0	0	0	. 0
$n_3$	0	0	0	0
$C_{i}$	0.5	0.5	0.5	0.75
$C_2$	0.85252	1	0.85252	1
F ₁	1	1	1	1
	0.85252	0.85252	0.79329	0.91771
23	0	0	0	1
<i>e</i> ₄	4	2	4	1
c _s	0	0	0	1
$C_{1a}$	0.5	0.5	0.5	0.75
$C_{2o}$	0.85252	ž 1	0.85252	1
$V_e(eV)$	-104.37986	-33.80733	-102.49036	-39.09538
$V_p(eV)$	20.85777	10.19898	21.11822	13.45505
T(eV)	35.96751	9.49831	36.20391	12.74462
$V_m$ (eV)	-17.98376	-4.74915	-18.10196	-6.37231
E(AOIHO) (eV)	0	-14.63489	0	-14.63489
$\Delta E_{H_2MO}(AOIHO)$ (eV)	-2.26759	-1.85836	0	-2.26758
$E_{T}(AOIHO)$ (eV)	2.26759	-12.77653	0	-12.36731
$E_{T}(H_{2}MO)$ (eV)	-63.27075	-31.63572	-63.27019	-31.63533
$E_r(atom-atom, msp^3.AO)$ (eV)	-2.26759	-2.26759	-3.71673	0
$E_r(MO)$ (eV)	-65.53833	-33.90295	-66.98746	-31.63537
$\omega \left(10^{15} \ rad \ / \ s\right)$	15.4421	12.3131	58.0664	28.9084
$E_{K}$ (eV)	10.16428	8.10471	38.22034	19.02803
$\overline{\overline{E}}_{D}(eV)$	-0.20668	-0.19095	-0.40965	-0.27301
$\overline{E}_{Kvih}$ $(eV)$	0.17897 [6]	0.14829 [48]	0.12523 [57]	0.39427 [56]
$\overline{E}_{asc}$ (eV)	-0.11720	-0.11680	-0.34704	-0.07587
$E_{mag}$ $(eV)$	0.14803	0.14803	0.14803	0.14803
$E_{T}(ciranp) (eV)$	-65.77272	-34.01976	-67.68154	-31.71124
$E_{initial}(c_4 AOIHO) (eV)$	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_s AOFHO) (eV)$	0	0	0	-13.59844
$E_D(cironp)$ (eV)	7.23317	4.74998	9.14198	3.32988

C4H4O Furan			,	-				(eV) 41.67782	1007 17			1							
			1		, ,	4			1		0.00023		1						
	-	1									50000	ı		Á					
table 15.2.78. The bond angle parameters of furan and experimental values [I]. In the calculation of θ, the parameters from the preceding angle were used. E. [atom - atom, mso ² , AO]	igle parame	eters of fur	ran and e	xperimental	values [1]. In the	e calculation	of $\theta_{\nu}$ , the parame	ters from th	e preceding	angle were	used, E.	is E. (atc	m-atom.n		A p				
angle A vicini	2c' Bond 1 (a ₀ )	2c' Bond 2 (a ₀ )	2c' Terminal Atoms	Econtombie Atom 1	Atom 1 Hybridization Designation	E Canlembic Atom 2	Atom 2 Hybridization Designation	C ₂ Atom í	C2 Atom 2	5	Č,	25	25		r o	9	(c) (cal.	6	Exp. θ
			(a ₀ )		(Table 15.3.B)		(Table 15.3.B)								5				=
O".)HZ	2.02241	2.57707	3.9328	-16.88873	15	-13.61806	0	0.80561	0.79329 Eq.	0.75	-	0.75	0.98470	0		1	=	117.02	115.9
$\angle C_{\mu}C_{\mu}H_{a}$									(15.150))				1				-		(furan)
ZH,C,C,	2.02241	2.66807	4 2269	-16.88873	>-	-15.95954										117.02	110.69 13.	132.29	i
	Т	-		7,	2	C,	٥	0.80561	0.85252	0.75	_	0.75	1.05822	0			12	128.09	128.0
ZH,C,C,	2.02241	2.60925	4.2269	-16.88873	15	-15.95954 C,	9	0.80561	0.85252	0.75	-	0.75	1.05822	0		$\dagger$	=	131 32	(mian)
ZH,C,C,	2.02241	2.60925	4.1312	-17.09334 C.,	81	-16.47951 C	11	0.79597	0.82562	0.75	-	0.75	1.03725	0			1 2		
ZC,C,H,						e				2					+	+	4	07.70	
0.537		-		-17.09334			i.		0.79329		1					125.76	107.01	127.23	(furan)
(" 1"777	2.60925	2.57707	4.2661	C,	18	-13.61806	0	0.79597	Eq. (15.150))				0.79463	-1.65376				10.69	110.7
".)O".)7	2.57707	2.57707	4.1231	-18,22713	30	-18.22713	30	0.74646	0.74646	-	-	-	0.74646	760301	+	+			(unian)
, ∠C,C,C,	2.60925	2,66807 4,2426	4.2426	-17.81791	26	-18 02252	2	07070	200		1	-	0.74040	0.0201-	+	-	106.25		(furan)

## THIOPHENE

Thiophene having the formula  $C_4H_4S$  comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the C-S-C functional group. The 1,3-butdiene moiety 5 comprises C-C, C=C, and CH functional groups. The CH, C-C, and C=C groups are equivalent to the corresponding groups of pyrrole and furan given in the corresponding sections.

The C-S-C functional group of thiophene is solved in a similar manner as that of the C-N-C group of pyrrole and the C-O-C group of furan. The solution of the C-S-C functional group comprises the hybridization of the 2s and 2p AOs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the C-S-C-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52).

In thiophene, the energy of sulfur is less than the Coulombic energy between the electron 15 and proton of H given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is  $c_2(benzeneC2sp^3HO) = 0.85252$  to match the double-bond character of the  $C2sp^3$  HOs, and the energy matching condition is further determined by the  $C_2$  parameter. Using the energy of S,  $E(S) = -10.36001 \, eV$  in Eq. (15.68) and the  $C2sp^3$  HO energy of  $E(C,2sp^3) = -15.76868 \, eV$  (Eq. (15.18) corresponding to S=2 in Eqs. (15.18-15.20), the 20 hybridization factor  $C_2$  of Eq. (15.52) for the C-S-C-bond MO is

$$C_2(S3p \text{ to aryl-type } C2sp^3HO) = \frac{E(S,3p)}{E(C,2sp^3)} = \frac{-10.36001 \text{ eV}}{-15.76868 \text{ eV}} = 0.65700$$
 (15.153)

 $C_{1o}$  is also given by Eq. (15.153). Furthermore,  $\Delta E_{H_2MO} \left(AO/HO\right)$  of the C-S-C- bond MO in Eq. (15.42) and  $E_T \left(atom-atom,msp^3.AO\right)$  in Eq. (15.52) are both -0.72457~eV per atom corresponding to -2.89830~eV in total. The energy contribution equivalent to that of 25 a methyl group (Eq. (14.151)) and that of the C-S-bond MO of thiols given in the corresponding section matches the energy of the sulfur atom to the  $C2sp^3$  HOs.

The symbols of the functional groups of thiophene are given in Table 15.279. The structure of thiophene is shown in Figure 67. The geometrical (Eqs. (15.1-15.5) and (15.42)),

intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of thiophene are given in Tables 15.280, 15.281, and 15.282, respectively. The total energy of thiophene given in Table 15.283 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.282 corresponding to functional-group composition of the molecule. The bond angle parameters of thiophene determined using Eqs. (15.79-15.108) are given in Table 15.284.

Table 15.279. The symbols of functional groups of thiophene.

Functional Group	Group Symbol
$C_a = C_b$ double bond	C = C
$C_b - C_b$	C-C
$C_a - S - C_a$	C-S-C
СН	СН

1.078 (thiophene) CH Group 1.53380 1.01120 1.15326 1.07021 Table 15.280. The geometrical bond parameters of thiophene and experimental values [J]. Parameter C = C C - S - C C - S - C Group Group 1.714 (thiophene) 1.74058 1.62766 1.72264 0.61671 1.423 (thiophene) C-C Group 1.77965 1.33404 1.17792 0.74961 1.370 (thiophene) C=C Group 1.45103 1.30463 1,38076 0.63517 0.89910  $a (u_o)$   $c' (a_o)$ Bond Length  $2c' \{A\}$ Exp. Bond
Length (A) $h,c(a_0)$ 

Table 15.281. The MO to HO intercept geometrical bond parameters of thiophene.  $R_i$  is an allkyl group and  $R_iR_i$ ,  $R_i$  are H or alkyl groups.  $E_T$  is  $E_T$  (atom - atom,  $mxp^3$ . AO). Bond

	Atom	$\begin{array}{c} E_{\tau} \\ \text{(eV)} \\ \text{Bond 1} \end{array}$	$\begin{array}{c} E_T \\ \text{(eV)} \\ \text{Bond 2} \end{array}$	$\begin{array}{c} E_r \\ \text{(eV)} \\ \text{Bond 3} \end{array}$	$E_{r}$ (eV) Bond 4	Final Total Energy $C2xp^3$	$\binom{r_{bitied}}{(a_0)}$	$\binom{r_{fined}}{(a_0)}$	$E_{Content}(C2sp^{1})$ (eV) Final	$\frac{E(C2sp^3)}{(eV)}$ Final	(°)	(°)	$\theta_2$	$\begin{pmatrix} d_i \\ (a_o) \end{pmatrix}$	(a ₀ )
$C-H\left(C_{a}H\right)$	ر. ً	-1.13380	-0.72457	o	0	-153.47406	0.91771	0.81549	-16.68412	-16,49326	84.49	15 50	44.74	1 00000	crato o
$C-H(C_bH)$	-ť	-1.13380	-1.13380	٥	6	-153 88378	122100	0 10507	17,0003				L.	1,007.1	0.07833
J = (H)J = J(H) = J	;				,	0700000	111160	0.79597	-17.09334	-16.90248	82.21	97.79	43.14	1.11914	0.10794
$C_n = (U)_n = C_n (U) = C_n$	۲,	-1.13380	-1.13380	0	0	-153.88328	17716.0	0.79597	-17.09334	-16.90248	91.57	88,43	42.49	1.31226	0.07177
$C_{n} = C_{h}(H)(H)C_{h} = C_{n}$	<u>"</u>	-1.13380	-1.13380	0	c	-153 88328	0.01771	20302.0	, , , , , , , , ,						111700
SC = C(H)	: :				,	0700000	22111	0.19391	-17.09334	-16.90248	136.36	43.64	59.86	0.72857	0.57606
1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	ا ر	-1.13380	-0.72457	0	0	-153.47406	17710	0.81549	-16.68412	-16.49326	137.14	42.86	60.85	0.70685	111111111111111111111111111111111111111
$C_{\bullet}S - C_{\bullet} = C_{\bullet}(H)$	ڻ ا	-1.13380	-0.72457	0	0	-153,47406	0.91771	0.81549	-16.68412	-16.49326	141 52	38.48	25.35	2000	2000
$C''S-C'_n=C_b(H)$	S	-0.72457	-0.72457	0	0		1 3201	0.83600	16 27400				200	076970	0.03840
							1000.1	o, esuco	10.27490	2	142.17	37.83	56.24	0,96733	0.66033

Table 15.282. The energy parameters (eV) of functional groups of thiophene.	rs (eV) of function	al groups of thiopl	iene.	
Parameters	C=C Group	C – C Group	C-S-C Group	CH Group
n,	2	1	2	1
$n_1$	0	0	0	0
п	0	0	0	0
C	0.5	0.5	5.0	0.75
ئ"	0.85252	1	0.65700	1
2,	1	-	1	. 1
c,	0.85252	0.85252	0.85252	0.91771
ూ	0	0	0	-
υ ⁷	4	2	4	1
ິນັ	0	0	0	1
<u>.</u>	0.5	0.5	6.0	0.75
ئ	0.85252	1	0.65700	1
V, (eV)	-104.37986	-33.80733	-96.78916	-39.09538
V, (eV)	20.85777	10.19898	16.71820	13.45505
T (eV)	35,96751	9.49831	27.80371	12.74462
V, (aV)	-17.98376	-4.74915	-13.90186	-6.37231
15 (no 110) (eV)	0	-14.63489	0	-14.63489
ΔΕ _{11,300} (30 110) (eV)	-2.26759	9£858:1-	-2.89830	-2.26758
$E_{r}(so\ io)\ (eV)$	2.26759	-12.77653	2.89830	-12.36731
$E_r(u,so)$ (eV)	-63.27075	-31.63572	-63.27080	-31.63533
$E_T(atom - atom, msp^3.AO)$ (aV)	-2.26759	-2,26759	-2.89830	0
$E_{\tau}(so)$ (eV)	-65.53833	-33.90295	-66.16903	-31,63537
$\omega \left(10^{15}  rad  I.s\right)$	15.4421	12,3131	10.3184	28.9084
$E_{K}\left( eV ight)$	10.16428	8.10471	6.79173	19.02803
$\overline{L}_{n}$ (eV)	-0.20668	-0.19095	-0.17058	-0.27301
$\overline{\overline{E}}_{\mathrm{Krit}}$ (eV)	0,17897 [6]	0.14829	0.08146	0.39427
$\overline{\mathcal{E}}_{ce}$ (eV)	-0.11720	-0,11680	-0.12985	-0.07587
Emg (eV)	0.14803	0.14803	0.14803	0.14803
$E_{T}(\iota_{im\phi})$ (eV)	-65.77272	-34.01976	-66.42873	-31.71124
Existed (cz. 110 110) (eV)	-14.63489	-14.63489	-14.63489	-14,63489
15 mind (c. 30 110) (cV)	0	0	0	-13.59844
En (comp) (cV)	7,23317	4.74998	7.88917	3,32988

Table 15.284. The bond angle parameters of thiophene and experimental	angle paran	neters of ti	hiophene a	and experim	ental values [1]. 1	in the calcula	values [1]. In the calculation of $\theta$ , the parameters from the preceding angle were used $E$ is $E \left( angle = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone = alone =$	rameters fro	m the prece	ding angle	were nsed	7. 7.	(atom = otc	m mem ³ 40)				
Atoms of Angle	2c' Band I (a ₀ )	2c' Bond 2 (a ₀ )	2c' Termical Atoms (a ₀ )	E Condanière Alam 1	Atom 1 Hybridization Designation (Table 15.3.B)	EConfondic Atom 2	Atom 2 Hybridization Designation	C ₂ Atom I	C ₂	5	Č	5	25	$E_T$ (eV)	) (o)	θ ₁ θ ₂ (°)	Cai. 9	Exp. 6
ZHC,S	2.02241	3,25533	4.6030	-15.55033		-10.36001	S	0.87495 Eq.	0.76144 (Eq.	0.75	0.76144 (Eq.	0.75	0.87495	0		-	119.58	
ZC,C,H,								(feerer)	10,140)		((07).C1	,			+		-	(thiophene)
JJHI	7 02741	7,0000	╆~	-16.68412		-15.95954									=	119.58 115.84	84 124,58	
4 - 4 - 4	2,02241	7.00007	4.1033	ڻ	14	۲,	و	0.81549	0.85252	0.75	_	0.75	1.04540				124.58	124.3
′′′′′′′′′′′′′′′′′′′′′′′′′′′′′′′′′′′′′	2.02241	2.60925	4.1633	-16.68412 C,	14	15.95954 C,	9	0.81549	0.85252	0.75	-	0.75	1.04540	0			127.57	_
ZH,C.,C.,	2.02241	2.60925	4.0825	-17.09334 C,	81	-16.68412 C,	14	0.79597	0.81549	0.75	-	0.75	1.02453	0			123 13	
ZC,C,H,															- -			1243
5 7 7 7				-17.81791					0.65700		000000	1			2	123.13 113.00	123.27	9
C, 14.72	2.60925	3.25533	4.9809	ΰ	27	-10.36001	vs	0.76360	Eq. (15.153))	-	Eq.	-	0.71030	-0.72457			115.84	115.5
ZC" SC"	3,25533	3.25533	4.7958	-16.68412	4	-16.68412	4	0.81549	0.81549	-	1	T-	0.81549	-1 85836	-	-	3	(unoparene)
2C,C,C,	2.60925	2.66807	4.4159	-16.88873	15	-18.02252	29	0.80561	0.75493	-	-	-	70000	Occupation of the second	+	+	2. 28	
									-	-	-	-	0.78027	-1.85836	_		113.60	(thiophene)

## **IMIDAZOLE**

Imidazole having the formula  $C_3H_4N_2$  comprises a conjugated system that is equivalent to pyrrole with one of the conjugated CH groups replaced by a nitrogen atom. The CH, NH, and C = C groups are equivalent to the corresponding groups of pyrrole, 5 furan, and thiophene where present. In addition, the nitrogen substitution creates a C-N=C moiety comprising C-N and N=C functional groups. The C-N bonding is the same as that of a tertiary amine except that the hybridization term  $c_2$  in Eqs. (15.42) and (15.52) is that of the amino group of aniline,  $c_2(arylC2sp^3HO\ to\ N) = 0.84665$  (Eq. (15.152)). The hybridization factor provides double-bond character to match the group to the  $\Delta E_{H,MO}(AO/HO)$  in Eq. (15.42) and 10 other orbitals of the molecule.  $E_T(atom-atom, msp^3.AO)$  in Eq. (15.52) are both -0.92918 eV (Eq. (14.513)). This matches the energy of the group to that of the contiguous N = C group wherein  $\Delta E_{H,MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom, msp^3.AO)$  in Eq. (15.52) are both -0.92918 eV (Eq. (14.513)) per atom of the double bond with aromatic character as in the 15 case of the prior heterocyclic compounds. As in the prior cases of pyrrole, furan, and thiophene,  $n_1 = 2$  and  $C_2$  and  $C_{2o}$  are the same as  $C_2$  (benzeneC2sp³HO) = 0.85252 (Eq. (15.143)) in Eqs. (15.42) and (15.52). To match the energy of the nitrogen to the  $C2sp^3$  HO,  $c_2$  of the N=C-bond MO is also given by Eq. (15.152). These parameters also provide an energy match to the C-N-C group.

As in the case of pyrrole, the C-N-C-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52). The hybridization factor  $c_2(arylC2sp^3HO\ to\ N) = 0.84665$  (Eq. (15.152)) matches the double-bond character of the  $C2sp^3$  HOs to the N atom of the NH group, and  $C_2$  and  $C_{20}$  in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143),  $C_2(benzeneC2sp^3HO) = 0.85252$ . Furthermore,  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) are both  $-0.92918\ eV$  (Eq. (14.513)) per atom corresponding to  $-3.71673\ eV$  in total.

The symbols of the functional groups of imidazole are given in Table 15.285. The structure of imidazole is shown in Figure 68. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of imidazole are given in Tables 15.286, 15.287, and 15.288, respectively. The total energy of imidazole given in Table 15.289 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.288 corresponding to functional-group composition of the molecule. The bond angle parameters of imidazole determined using Eqs. (15.79-15.108) are given in Table 15.290.

10 Table 15.285. The symbols of functional groups of imidazole.

Functional Group	Group Symbol	
$C_a = C_b$ double bond	C = C	
$N_b = C_c$ double bond	N = C	
$C_b - N_b$	C-N	
$C_a - N_a - C_c$	C-N-C	
$N_aH$ group	$N\!H$	
CH	CH	

						-		
	CH	Group	1.53380	1.01120	1,07021	1.076 (pyrrole)	1.15326	0.65928
	, HN	Group	1,24428	0.94134	0.996270	0,996 (pyrrole)	0.81370	0.75653
	C-N-C	Group	1.43222	1.29614	1.37178	1.370 (pyrrole)	0.60931	0.90499
permental values [1].	C-N	Group	1.82450	1.35074	1.42956		1,22650	0.74033
EIETS OF HINTUAZOIC AILU C	N=C	Group	1.44926	1.30383	1.37991		0.63276	0.89965
able 15.286. The geometrical bond parameters of influazore and experimental values 11	2=2	Group	1.45103	1.30463	1.38076	1.382 (pytrole)	0.63517	0.89910
Table 13.280, 1110	Parameter		a (a ₀ )	$c^*(a_b)$	Bond Length $2c'$ ( $A$ )	Exp. Bond Length $(A)$	h,c (a ₀ )	υ

Table 15,287. The MO to HO intercept geometrical bond parameters of imidazole. R, is an alkyl group and R, R', R'' are H or alkyl groups. E _T is E _T (atom - ottom, may 'Ale)	netrical bond	parameters of ii	midazole. R is	an alkyl group	md R,R',R" ar	e H or alkyl gr	oups. E ₇ is b	r (atom – aton	1,msp'AO}.	16 20/2	10	9	9
Bond	Atom	E,	ET	7. Y.	Er	Final Total	outral (	find	E-man (C2sp")	$E(C2sp^2)$	. G	ъ. Э	e, 2
		(ev) Bond I	(ev) Bond 2	Bond 3	Bond 4	(72 <i>xp</i> ³	(g°)	(a _o )	Final	(eV) Final	===	===	=
('-H ((',H)	ن ٔ	-1,13380	-0.92918	0	0	-153.67867	17710	0.80561	-16.88873	-16.69786	83.35	96.65	43.94
$C-H\left(C,H\right)$	C,	-1.13380	-0.46459	0	0	-153.21408	17710.0	0.82840	-16.42414	-16.23327	85.93	94.07	45.77
('-H (C,H)	ن	-0,92918	-0.92918	0	0	-153,47405	17716.0	0.81549	-16.68411	-16.49325	84,49	95.51	44.47
$C_{\mu} = (H)C_{\mu} - N_{\nu} = C_{\nu}$	ئ	-0.46459	-1.13380	0	0	-153.21408	17710	0.82840	-16.42414	-16.23327	90.36	89.64	42.49
$C_s = (H)C_s - N_s = C_s$	N,	-0.46459	-0.92918	o	0		0.93084	0.83885	-16.21953		91.32	88.68	43.14
$C_a = C_b(H)N_b = C_c$	ڻ	-1.13380	-0.46459	0	0	-153.21408	17710	0.82840	-16.42414	-16.23327	137.64	42.36	61.49
$HN_{r}C_{r}=C_{r}(H)$	·."	-1.13380	-0.92918	0	0	-153.67867	17710.0	0.80561	-16.88873	-16.69786	136.75	43.25	60,35
$C_c(H)N_s - C_s = C_k(H)$	ان "	-1,13380	-0.92918	0	0	-153,67867	17716,0	0.80561	-16.88873	-16.69786	138.54	41.46	60.19
$C_c(H)N_a - C_s = C_s(H)$	ν"	-0.92918	-0.92918	0	0		0 93084	0.81549	-16.68411		138.92	41.08	61.59
$N-H$ $(N_oH)$	χ,	-0.92918	-0,92918	0	0		0.93084	0.81549	-16.68411		117.34	9979	62.90
$(H)C_c - N_aC_a = C_b(H)$	ئ	-0.92918	-0,92918	0	0	-153,47405	17710.0	0.81549	-16.68411	-16.49325	138.92	41.08	61.59
$C_{\nu} = (H)C_{\nu}N_{\nu} = C_{\nu}$	ئن	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	137.31	42.69	60.92

805

0.60376

0.71784

0.61467

0.55678

0.59938

0.68147

0.67849

0.01939

0.00527

1.10452 1.06995 1.08953 1.34547 1.33135 0.69250

 $\begin{pmatrix} d_1 \\ a_0 \end{pmatrix}$ 

 $\begin{pmatrix} a_1 \\ a_0 \end{pmatrix}$ 

Table 15.288. The energy parameters (eV) of functional groups of imidazole.	rs (eV) of function	al groups of imida	izole.			
Parameters	C = C Group	N = C Group	$C \sim N$ Group	C-N-C Group	NH Group	CH Group
$n_1$	2	2	I	2	Į	-
$l_{\mathcal{U}}$	0	0	0	0	0	0
п,	0	0	0	0	0	0
5	0.5	0.5	5.0	0.5	0.75	0.75
C.	0.85252	0.85252	1	0.85252	0.93613	-
'চ	-	-	1	-1	0.75	
ั้ง	0.85252	0.84665	0.84665	0.84665	0.92171	17716.0
້ວ	0	0	0	0	1	1
່"ວ	4	4	2	4	1	1-1
<b>"</b>	0	0	0	0		
ر."	0.5	0.5	5.0	5.0	0.75	0.75
· .	0.85252	0.85252	-	0.85252	1	
V _c (cV)	-104.37986	-103.92756	-32.44864	-106,58684	-39.48897	-39.09538
V, (eV)	20.85777	20.87050	10.07285	20.99432	14.45367	13.45505
T (eV)	35.96751	35,85539	8.89248	37,21047	15.86820	12.74462
V, (eV)	-17.98376	-17.92770	-4.44624	-18.60523	-7.93410	-6.37231
$E(\omega m)$ (eV)	0	0	-14.63489	0	-14.53414	-14.63489
$\Delta \mathcal{L}_{H_{a}M_{b}}(A\sigma ma)(\mu V)$	-2.26759	-1.85836	-0.92918	-3.71673	0	-2.26758
Er (10.110) (eV)	2,26759	1,85836	-13.70571	3.71673	-14.53414	-12.36731
$E_{T}(u_{1}\omega)$ (cV)	-63.27075	-63.27100	-31.63527	-63.27056	-31,63534	-31.63533
$E_r(atom - atom, msp^3.AO)$ (eV)	-2,26759	-1.85836	-0,92918	-3.71673	0	0
$E_r(xr)$ (eV)	-65.53833	-65,12910	-32.56455	-66.98746	-31.63537	-31,63537
$\omega \left(10^{13} rad/s\right)$	15.4421	15.4704	21.5213	15.7474	48.7771	28.9084
$E_{K}$ (eV)	10.16428	10.18290	14.16571	10.36521	32.10594	19.02803
$\vec{E}_{p}$ (eV)	-0.20668	-0.20558	-0.24248	-0.21333	-0.35462	-0.27301
Exm (eV)	0.17897	0.20768	0.12944 [23]	0,11159	0.40696	0.39427
E (eV)	-0.11720	-0.10174	-0.17775	-0.15754	-0.15115	-0.07587
Emy (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{T}(\mathrm{irrup})$ (cV)	-65.77272	-65.33259	-32.74230	-67.30254	-31.78651	-31.71124
Emma (r. 10 110) (eV)	-14.63489	-14.63489	-14,63489	-14.63489	-14.53414	-14.63489
$E_{\rm insteal}(\epsilon, \omega m)$ (eV)	0	0	. 0	0	-13.59844	-13.59844
$E_D( ext{tionsp})$ (eV)	7.23317	6.79303	3.47253	8.76298	3.51208	3.32988
		!				

i values [2].	Relative Error	-0.00056
ed to the experimenta	Experimental Total Bond Energy (eV)	39.74106
ile 15.288 compar	Calculated Total Bond Energy (eV)	39.76343
e energies of Tab	СН	
ition and th	NH	-
ial eroup compos	C-N-C	
the function	C: – N	-
calculated using	N = C	-
ajes of imidazole	C=C	-
Takla 15 280 The rotal hand energ	Name	
Table 15 280	Formula	

ı	1		ı	ı	1		1			80	)7			Γ
Exp. θ (°)	117.4 (imidazole)	136,3 (imidazole)	122.9 (imidazole)	136.3 (imidazole)	133.2 (imidazole)	115.8 (imidazole)	110.4 (imidazole)	138.2 (fmidazole)	129.1 (imidazole)	106,3 (imidazole)	107.2 (fimidazole)	105.4 (imidazole)	109.8 (Imidazole)	
(°)	120,51	132.86	120.37	135.30	134.28	114.54	112.37	137.80	129.96	107.52	109.83	108.64	111.18	+
6		106,63				111.18		109.83						
θ ₁ ()		120.51				134.28		112.37						
θ, (°)										_				
E _T (eV)	0		0	0	0				0	-1,44915	-1.85836	-1.85836	-1.85836	
35	1.00435	ı	0.97435	96120'1	1.07647		0.96765		1.01912	0.82131	0.76360	0.77247	0.84958	
ઈ '	0.75		0.75	0.75	0.75	×	0.75		0.75		-	-	1	
5	-		-	_	-		_		-	-	-	1	-	
c ^t	0.75		0.75	0.75	0.75		0.75		57:0	1		1	1	-
C ₂ Atom 2	0.92171 Eq. (15.151))		0.82493 (Eq. (15,64))	0.86359	0.91771	ş	0.84665 (Eq.		0.86284 (Eq. (15.64))	0.79597	0.76360	0.77247	0.84665 (Eq. (15.152))	110.10011
C ₂ Atom l	17716.0		0.84665 (Eq. (15.151))	0,80561	0.85252		0.87495		0.84665 (Eq. (15.151))	0.84665 (Eq. (15.152))	0,76360	0,77247	0.85252	_
- Atom 2 Hybridization Designation (Table 15.3B)	z		13	4	_		z		9	18	26	25	z	
Eindonke Mon 2	-14,53414		-16.49325	-15.75493	-14.82575 C.		-14.53414		-15.76868	-17.09334 C,	-17.81791	-17.61330	-14.53414	
Atom I Hybridization Designation (Table 15.38)	-		z	15	9		9		z	z	26	23	9	
Et retomber Atom 1	-14.82575		-14.53414	-16.88873 C	-15,95954		-15.95954 C.		-14,53414	-14.53414	-17.81791	-17,61330	-15.95955	
2c' Terminal Atoms (a ₀ )	4.0166		3.8987	4.2895	4.2740		3.8471		4.0651	4.1952	4.2426	4.3128	4,3818	
2c' Bond 2 (a,)	2.59228		2.59228	2.60925	2,60925		2,59228		2.59228	2.60925	2.59228	2,70148	2,70148	
2c' Bond (	2.02241		1.88268	2.02241	2.02241		2,02241		1.88268	2.59228	2.59228	2.60766	2.60925	
Anons of Arabit 2 $c'$ 2 $c'$ 2 $c'$ Terminal Arabit 1 bload 2 Terminal Arabit 2 $c'$ Arabit 2 $c'$ Terminal Arabit 3 SS) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a_0$ ) ( $a$	ZHC,N,	ZC,C,H,	".J"NH7	ZH,C,C,	ZH,C,C,	ZN,C,H,	ZH,C',N,	ZN.C. H.	ZHIN C.	ZN,C,C,	ZC,N,C,	ZC. N,C,	ZC.,C,Nh	

### **PYRIDINE**

Pyridine has the formula  $C_5H_5N$  and comprises the benzene molecule with one CH group replaced by a nitrogen atom which gives rise to a C=N functional group. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in the 5 Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the C=N group which is also aromatic.

As in the case of the aromatic carbons of benzene, each pyridine  $C2sp^3$  HO initially has four unpaired electrons. Each C-H bond has two paired electrons with one donated from the H AO and the other from the  $C2sp^3$  HO. In pyridine the three N2p electrons are donated to the aromatic bond. Thus, as in the case of the C=C group, each C=N bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from the  $C2sp^3$  HO and the N2p AO of the participating carbon and nitrogen atoms, respectively.

The solution of the C=N functional group comprises the hybridization of the 2s and 2p AOs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. The C=N-bond MO is solved as a double bond with  $n_1=2$  in Eqs. (15.42) and (15.147). The hybridization factor  $c_2(C2sp^3HO\ to\ N)=0.91140$  (Eq. (15.116)) matches the double-bond character of the  $C2sp^3$  HO to the  $C2sp^3$  HO to the  $C2sp^3$  HO to the  $C2sp^3$  HO to the  $C2sp^3$  HO to the  $C2sp^3$  HO such that  $C2sp^3$  HO in order to match the nitrogen to the aromatic  $C2sp^3$  HO such that  $C2sp^3$  HO in Eq. (15.42). Furthermore,  $C2sp^3$  HO such that  $C2sp^3$  HO in Eq. (15.147) due to the charge donation from the  $C2sp^3$  HO atoms to the MO is  $C2sp^3$  HO in Eq. (15.147) due to the charge donation from the  $C2sp^3$  HO atoms to the MO is  $C2sp^3$  HO in Eq. (15.147) due to the charge donation from the  $C2sp^3$  HO atoms to the MO is  $C2sp^3$  HO in Eq. (15.147) due to the charge donation from the  $C2sp^3$  HO atoms to the MO is  $C2sp^3$  HO in Eq. (15.147) due to the charge donation from the  $C2sp^3$  HO atoms to the MO is  $C2sp^3$  HO in Eq. (15.147) due to the charge donation from the  $C2sp^3$  HO atoms to the MO is  $C2sp^3$  HO in Eq. (15.147) and the charge donation from the  $C2sp^3$  HO atoms to the MO is  $C2sp^3$  HO in Eq. (15.147) due to the charge donation from the  $C2sp^3$  HO atoms to the MO is  $C2sp^3$  HO in Eq. (15.147) and  $C2sp^3$  HO in Eq. (15.147) and  $C2sp^3$  HO in Eq. (15.147) and  $C2sp^3$  HO in Eq. (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.147) and (15.14

given by Eqs. (15.146) and (15.147), respectively, with  $f_1 = 0.75$ . The breakage of the *CNC* bonds results in three unpaired electrons on the N atom. Thus, the corresponding  $E_{mag}$  given by Eq. (15.60) was normalized for the two bonds per atom and for  $f_1 = 0.75$  and was subtracted from the total energy of the C=N-bond MO in Eq. (15.147). The pyridine vibrational energies are similar to those of benzene [60]; thus, the value for benzene was used.

The symbols of the functional groups of pyridine are given in Table 15.291. The corresponding designation of the structure is shown in Figure 69. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), 10 (15.17-15.56), and (15.146-15.147)) parameters of pyridine are given in Tables 15.292, 15.293, and 15.294, respectively. The total energy of pyridine given in Table 15.295 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.294 corresponding to functional-group composition of the molecule. The bond angle parameters of pyridine determined using Eqs. (15.79-15.108) are given in Table 15.296.

Table 15.291. The symbols of functional groups of pyridine.

15

Functional Group	Group Symbol
CC (aromatic bond)	$C \stackrel{3e}{=} C$
CH (aromatic)	CH
$C_a \stackrel{3e}{=} N$	$C {=} N$

i values [1].	C = N Group	1.47169	1.27073	1.34489	1,340	(pyridine)	0.74237	0.86245
pyridine and experimenta	C:H Group	1.60061	1.03299	1.09327	1.084	(pyridine)	1.22265	U 64537
able 15.292. The geometrical bond parameters of pyridine and experimental values [1]	Croup	1.47348	1,31468	1.39140	1.394	(pyridine)	0.66540	5,000,0
able 15,292. The geom	Parameter	a (a ₀ )	$c$ , $(a_o)$	Bond Length 2c' (A)	Exp. Bond Length	( <del>V</del> )	$b,c$ $(a_o)$	

Table 15.293. The MO to HO intercept geometrical bond parameters of pyridine. $E_r$ is $E_r(ann-ann,msp^3.AO)$	netrical bon	d parameters of	pyridine. $E_T$ is	$E_{\tau}(atom - atom$	$n, msp^3. AO$ .			 				
Bond	Atom	Er	E	ET	$E_T$	Final Total	Faired	Final	$E_{color}(C2sp^3)$	$E(C2sp^3)$	ιθ.	θ
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C2sp³	(a ₀ )	$(a_0)$	(eV) Final		©	<b>©</b>
C-H (C,H)	ئی	-0.54343	-0.85035	-0.56690	0	-153.57636	17716.0	0.81052	-16.78642	-16.59556	76.35	103.65
C-H $(C,H)$	ئن	-0.85035	-0,85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58
$(H)C_b(H)C_s = NC_s$	ڻ	-0.85035	-0.54343	-0.56690	0	-153,57636	17710.0	0.81052	-16.78642	-16,59556	128.54	51.46
$(H)C_{k}(H)C_{k}=NC_{k}$	×	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39
$(H)C_{\kappa} = C_{\kappa}(H)N$	ڻ	-0 54343	-0.85035	-0.56690	0	-153.57636	0,91771	0.81052	-16.78642	-16.59556	134.85	45.15
$(H)_{C_{\mu}} \stackrel{r}{=} C_{\mu}(H)_{N}$	ڻ	-0.85035	-0.85035	-0.56690	0	-153.88327	17716.0	0.79597	-17,09334	-16.90248	134,24	45.76

810

0.55533

0.75935

58.98

0.55656

0.71418

1,22423

38.84

 $\begin{pmatrix} d_1 \\ a_0 \end{pmatrix}$ 

(°)

Table 13.294. The energy parameters (eV) of functional groups of pyridine	(eV) of functional groups of	f pyridine.	
Parameters	C ≡ C Group	Crup Group	C=N Group
Ji	0.75		0.75
$n_1$	2	-	2
$n_2$	0	0	0
$n_3$	0	0	0
C.	6.5	0.75	0.5
$C_2$	0.85252	-	0.91140
ار.	1	1	
$c_2$	0.85252	0.91771	0.91140
6,3	0	-	0
3	3		
50	0		0
ر!»	0.5	0.75	0.5
( ;,	0.85252	1	0.91140
V, (eV)	-101.12679	-37.10024	-102.01431
V, (eV)	20.69825	13.17125	21.41410
T (eV)	34.31559	11.58941	34.65890
V _{ss} (eV)	-17.15779	-5.79470	-17.32945
E(30-110) (eV)	0	-14.63489	0
$\Delta E_{H_2M_0}$ (so m) (eV)	0	-1.13379	0
$E_T(x_U no) (eV)$	0	-13.50110	0
$E_T(n_2, \omega)$ (eV)	-63.27075	-31.63539	-63.27076
$E_T(atom - atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-1.44915
$E_T(\text{ing})$ (eV)	-65.53833	-32.20226	-64.71988
$\omega \left(10^{15} rad/s\right)$	49.7272	26.4826	43.6311
$E_{\kappa}$ (eV)	32.73133	17.43132	28.71875
$E_{\nu}$ (eV)	-0.35806	-0.26130	-0.33540
$E_{\lambda,vir}(aV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.19649
$\overline{L}_{ac}$ (eV)	-0.25982	-0.08364	-0.23715
$E_{ang}$ $(eV)$	0.14803	0.14803	0.09457
L'T (tient) (cV)	-49.54347	-32.28590	-48.82472
E 10 110 (cV)	-14.63489	-14.63489	-14.63489
Englad (c. 10 HO) (eV)	0	-13.59844	0
$E_D( ext{tinop})$ $(eV)$	5.63881	3.90454	4.92005
			!

Table 15.295. The total bond energies of pyridine calculated using the functional group composition and the energies of Table 15.294 compared to the experimental relations of Table 15.294 compared to the experimental relations of the experimental relations of Table 15.294 compared to the experimental relations of Table 15.294 compared to the experimental values [2]. I. Calculated Roman Region and Relative Error Group (eV) (eV) (eV) (eV) (eV)

Table 15.296. The bond angle parameters of pyridine and experimental values [1]. $E_r$ is $E_r$ ( $a_{com} - a_{com_s} n_{sp}^3$ , $AO$ ).	ıgle paramet	ters of pyri	idine and	experimental	I values [1]. $E_r$ is	$E_{\tau}(atom-at$	$(om, msp^3.AO)$ .												
Atens of Angle	2c' Band I (a _n )	2c' Hond 2 (a ₀ )	2c' Terminal Aloms (a _p )	F. Centouske Atom [	Atom 1 Hybridization Designation (Table 15.3B)	Ecalonine Atom 2	Atom 2 Hybridization Designation (Table 15 3B)	C ₂	C ₂	ŭ	7,	, 5	<b>3</b>	$E_T$ (eV)	9 (0)	9 (0)	(°)	Cal. θ (°)	Exp. $\theta$ (°)
ZXXX'' (aromatic)	2.62936	2.62936	4.5585	2.62936 2.62936 4.5885 -17.17218	70	-17.17218	20	0.79232	0.79232	_	_		0.79232	-1.85836			122	120,19	120 [50-52] (benzene) 118.3 (pyridine)
110.07																			(pyridine)
(aromatic)																120.19		16'611	120 [50-52] (benzene)
77.77									001140	+			1		-	-		_	(pyridine)
ZHC., IV	2.06598	2.54147	3.9497	2.06598 2.54147 3.9497 -14.82575	_	-14.53414	z	17716.0	S E	0.75		0,75	0.99312	0			_	117.65	115.9
ZNC.,C.,	2.54147	2.62936	4.5607	2.62936 4.5607 -14.53414	Z	-16.52644	12	0.91140 Eq.	0.82327	-	-	-	0.86734	-1 44015	-	-	+	ì	(pyridine)
.//. W	20,103.0	1						(15.116))						2722			<u>-</u>	67.79	(pyridine)
, Wa 🕶	7,34147	4.34147	4,3339	-17.71560	24	-17.71560	25	0.76801	0.76801		-		0.76801	-1,85836	-		=	117.00	116.8
								-		-	-		-	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		-		200	

## **PYRIMIDINE**

Pyrimidine has the formula  $C_4H_4N_2$  and comprises the pyridine molecule with one additional CH group replaced by a nitrogen atom which gives rise to a second C=N functional group that is equivalent to that of pyridine given in the corresponding section. The aromatic C=C and C-H functional groups are also equivalent to those of pyridine and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the C=N group which is also aromatic.

The symbols of the functional groups of pyrimidine are given in Table 15.297. The corresponding designation of the structure is shown in Figure 70. The geometrical (Eqs. 10 (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyrimidine are given in Tables 15.298, 15.299, and 15.300, respectively. The total energy of pyrimidine given in Table 15.301 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.300 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrimidine determined using Eqs. (15.79-15.108) are given in Table 15.302.

Table 15.297. The symbols of functional groups of pyrimidine.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH
$C_{a,b,d} \stackrel{3e}{=} N$	$C \stackrel{3e}{=} N$

ntal values   11.	C=N Groun	1.47169	1.27073	1.34489	1.340 (pyrimidine)	0.74237	0.86345
pyrimidine and experime	C'H Group	1.60061	1.03299	1.09327	1.084 (pyridine)	1.22265	0.64537
radic 15.230. The geometrical bond parameters of pyrimidine and experimental values 11	ortho	1.47348	1.31468	1.39140	1.393 (pyrimidine)	0.66540	0.89273
1 apric 12.279. 1116 gcul	Parameter	a (a _o )	$c'(a_0)$	Bond Length $2c'\left( \hat{A}  ight)$	Exp. Bond Length $(A)$	$b,c$ $(a_o)$	a

Table 15.299. The MO to HO intercept geometrical bond parameters	netrical bon	d parameters of	pyrimidine. $E_{_T}$	of pyrimidine. $E_T$ is $E_T \{alom - alom, msp^3, AO\}$	tom, msp³.AO).									
Bond	Atom	E _T (eV) Bond I	$E_r$ (eV) Bond 2	E _T (eV) Bond 3	E _T (eV) Bond 4	Final Total Energy C.2sp³ (eV)	$\binom{r}{m_{0}}$	(a ₀ )	$E_{Constan}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	(0)	θ (°)	(°)	$\begin{pmatrix} d_1 \\ (a_0) \end{pmatrix}$
$C-H\left( \mathbb{C}_{r}H\right)$	ن"	-0 54343	-0.54343	-0.56690	o	-153.26945	17710	0.82562	-16.47951	-16.28864	78.27	101.73	41.39	1,20084
$C - H\left(C_{k,d}H\right)$	ບໍ່ ບັ	-0.54343	-0.85035	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	76,35	103,65	40.11	1.22423
C-H (C,H)	ن٠	-0.85035	-0.85035	-0.56690	0	-153,88327	17716.0	0.79597	-17.09334	-16,90248	74.42	105.58	38.84	1.24678
$(H)C_{c}(H)C_{s}=N_{s}C_{s}$ $(H)C_{c}(H)C_{s}=N_{s}C_{s}$	ີ ບ້	-0.85035	-0,54343	-0.56690	0	-153,57636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0.76572
$(H)C_c(H)C_b = N_bC_a$ $(H)C_c(H)C_d = N_aC_a$	× ×	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130,61	49.39	60.97	0.71418
$(H)C_{c}(H)C_{t}N_{s}^{N}=C_{s}(H)$ $(H)C_{c}(H)C_{s}N_{s}=C_{s}(H)$	ن "	-0 54343	-0.54343	-0.56690	0	-153.26945	0.91771	0.82562	-16.47951	-16.28865	129.26	50.74	59.44	0.74824
$(H)_{C_{\varepsilon}}(H)_{C_{\varepsilon}N_{\varepsilon}} = C_{\varepsilon}(H)$ $(H)_{C_{\varepsilon}}(H)_{C_{\varepsilon}N_{\varepsilon}} = C_{\varepsilon}(H)$	× × ×	-0,54343	-0,54343	. 0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418
$N_{\sigma}(H)C_{s} = C_{\sigma}(H)C_{s}$ $N_{\rho}(H)C_{s} = C_{\sigma}(H)C_{s}$	ن	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935
$N_{\mu}(H)C_{\mu} = C_{\nu}(H)C_{\mu}$ $N_{\mu}(H)C_{\mu} = C_{\nu}(H)C_{\mu}$	ت ^ن ن ^۳	-0.85035	-0.54343	-0,56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	134.85	45.15	59.72	0.74304

814

0.16785

 $\begin{pmatrix} d_{\lambda} \\ a_{0} \end{pmatrix}$ 

	ر ال	CH	C=X
	Group	Group	Group
	0.75	-	0.75
1000	2	_	2
	0	0	0
	0	0	0
	5.0	0.75	0.5
	0.85252	1	0.91140
	1	1	
	0.85252	17716.0	0.91140
	0	1	0
	3	-	3
	0	-	0
	0.5	0.75	0.5
	0.85252		0,91140
	-101.12679	-37.10024	-102.01431
	20.69825	13.17125	21.41410
	34.31559	11.58941	34.65890
	-17.15779	-5.79470	-17.32945
E(.to 110) (eV)	0	-14.63489	0
ΔΕ _{π,310} (.10 110) (eV)	0	-1.13379	0
$E_{\tau}(\omega m)$ (eV)	0	-13,50110	0
E_ (11,20) (eV)	-63.27075	-31.63539	-63.27076
$E_T(atom - atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-1,44915
$\mathcal{E}_{T}(\iota_{R})$ (eV)	-65.53833	-32.20226	-64.71988
ω (1013 rad Is)	49.7272	26.4826	43.6311
	32.73133	17.43132	28.71875
	-0.35806	-0.26130	-0.33540
	0.19649	0,35532 Eq. (13,458)	0.19649 [49]
	-0.25982	-0.08364	-0.23715
	0.14803	0,14803	0.09457
$E_T(a_{min})$ (eV)	-49.54347	-32.28590	-48.82472
E mad (c. 10 110) (cV)	-14.63489	-14.63489	-14.63489
E (c. 10 10) (eV)	0	-13,59844	0
(1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1	10000		-0000

Formula	Name	<i>S</i> = <i>C</i>	н.э	C≈N Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Refative Error
T'N'S	Pyrimidine	2	4	<b>*</b>	46.57597	46,51794	-0.00125

		[E] n n n	T 6 7	=	_	<u>ē</u>	-
	Exp. 8	120 [50-52] (benzene) 118.3 (pyridine) 118.5 (byridine)	120 [50-5 (benzene 121.3 (pyridin	115.9 (pyñdine)	123.9 (pyńdine)	115.5 (pyrimidine)	127.6
	Cal. $\theta$	120.19	19.91	117.65	123.76	117.09	128.73
	ε _θ (ο)						
	(e)		120.19				
	o, ©						
	E _r (eV)	-1.85836		9	-1,44915	-1.85836	-1.85836
	73	0.79232	i.	0.99312	0.86734	0.76801	0.87495
	เง้า	~		0.75	(0)	-	-
	ပ်	_		-	1	-	1
	ď	-		0.75	1	ı	1
	C ₂ Aton 2	0.79232		0.91140 Eq. (15.116))	0.82327	0.76801	0.87495
	C ₂ Atom (	0.79232		0.91771	0.91140 Eq. (15.116))	0.76801	0.87495
-dom, msp³.AO}.	Atom 2 Hybridization Designation (Table 15.38)	20		N	13	24	٣
l experimental	Ecolomic Aton 2	-17.17218		-14.53414	-16.52644	-17.71560	-15.55033
	Atom I Hybridization Designation (Table 15.3B)	20		-	Z	. 24	٣
	Liverbarde Atom (	-(7,17218		-14.82575	-14,53414	-17,71560	-15.55033
nidine an	2c' Terminal Atoms (a ₀ )	4.5385		3.9497		4.3359	4.5826
s of pyrin	2c' !‱d2 (α _μ )	2.62936 4.5385		2,54147 3.9497	1.62936 4.5607	2.54147	2,54147 4,5826
le parameter	2c' Bwnd 1 (a ₀ )	2.62936		2.06598	2,54147	2,54147	2,54147
Table 15.302. The bond ang	Atoms of Angle	Z(Y; (? (aromatic)	Δ('C'H (aromatic)	ZHCN	ZNC:C	ZCNC.	ZNC:N

#### **PYRAZINE**

Pyrazine has the formula  $C_4H_4N_2$  and comprises the pyrimidine molecule with para rather than ortho aromatic nitrogen atoms. The C=N functional group is equivalent to that of pyrimidine and pyridine given in the corresponding sections. The aromatic C=C and C=C and functional groups are also equivalent to those of pyrimidine, pyridine, and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the C=N group which is also aromatic.

The symbols of the functional groups of pyrazine are given in Table 15.303. The corresponding designation of the structure is shown in Figure 71. The geometrical (Eqs. 10 (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyrazine are given in Tables 15.304, 15.305, and 15.306, respectively. The total energy of pyrazine given in Table 15.307 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.306 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrazine determined using Eqs. (15.79-15.108) are given in Table 15.308.

Table 15.303. The symbols of functional groups of pyrazine.

Functional Group	Group Symbol	
CC (aromatic bond)	C = C	
CH (aromatic)	$C\!H$	
$C_a = N$	C = N	

							_
I values [1].	C=N Group	1,47169	1.27073	1.34489	1.403 (pyrazine)	0.74237	0.86345
Table 15 304 The reometrical bond parameters of pyrazine and experimental values [1].	CH Group	1.60061	1.03299	1.09327	1,115 (pyrazine)	1,22265	0.64537
etrical bond parameters of	2=2 2=2	1.47348	1,31468	1.39140	1.339 (pyrazine)	0,66540	0.89223
Table 15 304 The reome	Parameter	a (a ₀ )	c' (a,)	Bond Leneth 2c' (A)	Exp. Bond Length	h,c (a,)	

Troops transport CII - Co to the way and the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the c	mod leaving	d parameters of	ers of pyrazine. E. is E. atom - atom, msp .AU	$E_{\tau}$ atom $-$ atoi.	", msp .40 j.					-		ľ		7
Table 15,305. The MO to HO intercept geometrical pour parents	ton ton ton	, branch			1	Ting Total	,		E. (C2sp)	$E(C)_{SD}^{3}$	θ,	ъ-	-r	z ¯
Bond	Atom	(eV)	E _T (eV) Bond 2	(eV) Bond 3	$\frac{E_7}{(eV)}$ Bond 4	Energy C2sp ³	$a_{\rm o}$	$(a_0)$	(eV) Final	(eV) Final	(0)	<u> </u>	<u> </u>	(a ₀ )
						(eV)						103.66	11.04	1 22423
			20000	0 56600	G	-153,57636	17710	0.81052	-16.78642	-16,59556	76.35	103.63	77.00	
(L-H(CH))	۔ ت	-0,54343	-0,85035	050050	·						1	7	57 63	0.76572
	,	0.0000	0.54343	06995 0-	0	-153.57636	17716.0	0,81052	-16.78642	-16,59556	128.54	31.40	78.07	
(H)C(H)C = NC	- ار	-0,83033	CFCFC,U-							1	13001	40.30	2009	0.71418
p. (-) (-)	;	2000	0.54343	0	0		0.93084	0.85503	-15.91261		130.01	4473	, ,	
H C(H)C=NC	≥.	c+c+c'n-	27.57								2070	31.37	50.72	0.74304
30	;	0 05035	.0 54143	-0.56690	•	-153.57636	0.91771	0.81052	-16.78642	-16.59556	134,83	C1:C4		
N(H)C  = C (H)N	'ن 	ccoco'o-												
/ \p p /														

Table 15.306. The energy parameters (eV) of functional groups of pyrazine	<ul> <li>V) of functional groups of</li> </ul>	pyrazine.	
Parameters	, C	CH	\ C = \ C
7	0.75	1	0.75
lu l	2	-	2
n,	0	0	0
<i>n</i> ,	0	0	0
C,	5.0	0.75	0.5
5	0.85252		0.91140
$c_{\rm l}$	_	1	1
$c_2$	0.85252	0.91771	0.91140
[c]	0	-	. 0
$c_4$	3	1	3
c _s	0	1	0
ري ا	9.5	0.75	0.5
(2)	0.85252	1	0.91140
V, (eV)	-101.12679	-37.10024	-102.01431
$V_{\mu}$ (eV)	20.69825	13.17125	21.41410
T' (eV)	34,31559	11.58941	34.65890
V,, (eV)	-17.15779	-5.79470	-17.32945
E(30 110) (eV)	0	-14.63489	0
$ \Delta E_{n_2 NO}(M HO) (eV)$	0	-1.13379	0
$E_T(\omega)$ (eV)	0	-13.50110	0
$E_T(\mu_1 \lambda \sigma)$ ( $\sigma V$ )	-63,27075	-31,63539	-63,27076
$E_T(atom - atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-1.44915
$E_{\tau}(\iota \kappa)$ $(eV)$	-65,53833	-32.20226	-64.71988
$\omega \left(10^{15} rad I.s\right)$	49.7272	26.4826	43.6311
$E_{\mathcal{E}}(eV)$	32.73133	17,43132	28.71875
$\vec{E}_o$ (eV)	-0.35806	-0.26130	-0.33540
$\overline{E}_{kirb}$ $(eV)$	0.19649	0.35532 Eq. (13.458)	0.19649
$\vec{E}_{\omega c}$ (eV)	-0.25982	-0.08364	-0,23715
$E_{\text{mag}}(eV)$	0.14803	0.14803	0.09457
$E_{\tau}$ (charg) (eV)	-49.54347	-32.28590	-48.82472
$E_{\text{initial}}(\epsilon_i, \omega \cdot m)$ (eV)	-14.63489	-14.63489	-14.63489
E 100 1 (c. 10 10) (cV)	0	-13,59844	0
$I_{\mathcal{I}_{I_{i}}}^{r}(\epsilon_{imp})$ (eV)	5.63881	3.90454	4.92005

Table 15.307. The total bond energies of pyrazine calculated using the functional group composition and the energies of Table 15.306 compared to the experimental values [2]. The formula Name C = C CH Total Bond Energy Total Bond Energy Total Bond Energy Relative Error Group CHAN Pyrazine C = C CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN CHAN

Administration of the bound angle parameters of pyrazine and experimental values [1].					ı														
1.7	2c' Bond 1 (a ₀ )	2c' Bond 2 (a ₀ )	Zc' Ternumal Atoms (a ₀ )	Econtombic Atom 1	Atom I Hybridization Designation (Table 15.3B)	Ecalombe Atom 2	Aton 2 Hybridization Designation	$C_2$ Atom 1	C ₂	ڻ-			`&	$E_T$ (eV)	θ (0)	θ ₁ (°)	Cal. 6	θ Exp. θ (°)	θ
ZCCC (aromatic)	2,62936	2,62936	4.558.5	-17.17218	20	-17.17218	20	0.79232	0.79232	-	-	-	0.79232	-1.85836			120	120 [50-52] (benzene) 118.3 (pyridine) [18.5	-52]
ZCCH (aromatic)															27	120.19	16.611		ne) -52]
N.JHZ	2.06598		2,54147 3,9497	-14.82575	_	-14.53414	Z	17716.0	0.91140 Eq.	0.75	-	0.75	0.99312	0			117.65		(au
НЭ.Э						į.			((011.01)						=	211	- -	_	(a)
ZNCC	2,54147	2,62936	4.4045	-14.53414	z	-17.09334	7	0.91140 " Eq.	0.79597	-	-	-	0.85368	-1.44915		10.011	116.81	(pyrazine)	9 19
ZCNC	2.54147	2,54147 2,54147	4,3359	-17.71560	24	-17.71560	24	0.76801	0.76801	-	-	-	0.76801	1 05030	-	-			e

## **QUINOLINE**

Quinoline has the formula  $C_9H_7N$  and comprises the naphthalene molecule with one CH group replaced by a nitrogen atom which gives rise to a C=N functional group. The aromatic C=C and C-H functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the C=N group which is also aromatic. The C-C functional group is also equivalent to that of naphthalene. The bonding in quinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the C=N group is equivalent to that of pyridine, pyrimidine, and pyrazine as given in the corresponding sections.

The symbols of the functional groups of quinoline are given in Table 15.309. The corresponding designation of the structure is shown in Figure 72. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of quinoline are given in Tables 15.310, 15.311, and 15.312, respectively. The total energy of quinoline given in Table 15.313 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.312 corresponding to functional-group composition of the molecule. The bond angle parameters of quinoline determined using Eqs. (15.79-15.108) are given in Table 15.314.

Table 15.309. The symbols of functional groups of quinoline.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH
$C_b - C_h$ (bridging bond)	C-C
$C_{a,d} = N$	$C \stackrel{3e}{=} N$

Table 15.310. The geom	Table 15.310. The geometrical bond parameters of quinoline and experimental values [1]	f quinoline and experiment	al values [1].	
Parameter	C=C Group	CH Group	C – C Group	C = N Group
a (a ₀ )	1,47348	190091	1.75607	1.47169
c' (a ₀ )	1,31468	1.03299	1.32517	1.27073
Bond Length 2c' (A)	1.39140	1.09327	1.40250	1.34489
Exp. Bond Length (A)	1.40 (avg.) (naphthalene)	1,101 (benzene)	1.42 (naphthalene)	1.340 (pyridine)
h,c (a _b )	0.66540	1.22265	1,15226	0.74237
6	0.89223	0.64537	0.75462	0.86345

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atom, msp³.	
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Table 15.311. The MC	
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		E	l	$E_T$	$E_T$	Final Total Energy	Feeting		$E_{Contout}(C2sp^3)$	$E(C2sp^3)$	.0	ø 3	θ,	$d_1$	, d
		(eV) Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	$C2sp^3$ (eV)	(a _o )	$(a_b)$	(ev) Final	(eV) Final	<b>.</b>	(_)	(,)	(a ₀ )	(0°)
	ن ا	-0.85035	-0.54343	-0.56690	. 0	-153.57636	17716.0	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1,22423	0,19124
<u>  _</u>	U ^t	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17,09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
	ڻ'	-0.85035	0,54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165
	ئن	-0.85035	-0,85035	-0.56690	0	-153,88327	17716.0	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
<u> </u>	رن	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16,80989	-16,61903	134.81	45.19	59,66	0.74430	0.57038
	ڻ	-0.85035	-0.54343	-0.28345	0	-153,29292	0,91771	0.82445	-16,50298	-16.31211	135.42	44.58	60.42	0.72743	0.58725
L.	٠,	-0.85035	-0.54343	-0,56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0 76572	0.50501
	2	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261	**	130.61	49.39	26'09	0.71418	0.55656
	ر.'	-0.85035	-0.54343	-0,28345	0	-153,29291	17710.0	0.82445	-16.50297	-16.31211	129.21	50.79	59,38	0.74960	0.52113
ļ	ن	-0.85035	-0.85035	-0.28345	0	-153,59983	0.91771	0.80939	-16.80989	-16.61903	95.01	84,99	44.41	1.25451	0.07066
<u> </u>	ر ا	-0.85035	-0.54343	-0 28345	0	-153,29292	17716.0	0.82445	-16 50298	-16.31211	16.31	83.69	45.33	1.23456	0.09061

Parameters	Ciec Group	Group	C-C Group	C = N Group
f	0.75	-		0.75
u l	2	-	1	2
n,	0	0	0	0
น์	0	0	0	0
5	0.5	0.75	0.5	5:0
	0.85252	-	1	0.91140
2	-	-	.1	1
ย์	0.85252	0.91771	0.85252	0,91140
ร์	0	1	0	0
ਬੌ	3	1	2	3
້	0	1	0	0
C.	0.5	0.75	0.5	5'0
7.3	0.85252	_	1	0.91140
V _c (aV)	-101.12679	-37,10024	-34.43791	-102.01431
V, (eV)	20.69825	13.17125	10.26723	21.41410
T (eV)	34.31559	11.58941	9.80539	34,65890
V,, (eV)	-17.15779	-5.79470	-4.90270	-17.32945
E(40 10) (aV)	0	-14.63489	-14.63489	0
$\Delta E_{n_1,n_2}(n_0 n_0)$ (eV)	0	-1.13379	-1.13379	0
$E_T(\omega m)$ (eV)	0	-13.50110	-13.50110	0
$E_T(u, wo)$ (eV)	-63.27075	-31.63539	-31.63529	-63.27076
$E_T(atom - atom, msp^3, AO)$ (eV)	-2,26759	-0.56690	-0.56690	-1.44915
$E_{r}(\iota \iota \sigma) \; (eV)$	-65.53833	-32.20226	-32.20226	-64.71988
$\omega \left(10^{15} rad / s\right)$	49,7372	26.4826	23.6343	43.6311
$E_{\rm K}$ ( $eV$ )	32.73133	17.43132	15.55648	28.71875
$\vec{E}_n$ (aV)	-0.35806	-0.26130	-0.25127	-0.33540
$\overline{E}_{kirt}$ $(eV)$	0.19649	——————————————————————————————————————	0,12312	0.19649
E (eV)	-0.25982	-0.08364	-0.18971	-0.23715
$E_{mg}$ (eV)	0.14803	0.14803	0.14803	0.09457
$E_{T}(imp)$ (eV)	-49.54347	-32.28590	-32.39198	-48.82472
Emms (c. 40 110) (eV)	-14.63489	-14.63489	-14.63489	-14.63489
E (1911) (4. 10 10) (eV)	0	-13.59844	0	0
E. (circus) (eV)	5 63881	3 90454	3 12220	40000

12 compared to the experimental values [2]. I	[ [ ] ]
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	$E_T$ (eV)	7 05036	-I.63630		
	<b>*</b> 2*	0.70733	0.13634		
ines [2]. [	ម	-			,
Relative Error	5	-			-
ergy R	5	-			-
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Energy 53	C ₂ Atom I	0.79232			0.78050
Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Calculated   Cal	Atom 2 Hybridization Designation (Table 15.3B)	20			24
C = N $Group$ $C = N$ $C = N$ $C = N$ $C = N$	Ermonesc Atom 2	-17.17218			-17.71560
Formula Name $C_{=C}^{3c}$ $CH$ $C_{=C}^{C}$ $C_{=M}^{3c}$ Total B Group Group Group Group $R$ $T$ 1 2 85  Table 15.314. The bond angle parameters of quinoline and experimental values [1]. $E_T$ is $E_T$ (atom — atom, mxp ³ .AO).	Atom I Hybridization Designation (Table 15.3B)	20			77
C.H. 7	Ecatonic Aum 1	2.65034 4.5585 -17.17218		ALCEN TI.	01304.71
C = C 8 noline and	- 2c' Terminal Alonis (a ₀ )	4.5585		4 38 18	
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Quinbline Calinoline 5.314. The bond ang		ZC.C.C	HJJJ7	ZC, NC	, ,
Formula C ₂ H ₂ N Table 15.31		`	7	۷ 	

# ISOQUINOLINE

Isoquinoline has the formula  $C_9H_7N$  and comprises the naphthalene molecule with one CH group replaced by a nitrogen atom which gives rise to a C=N functional group. Isoquinoline is also equivalent to quinoline with the nitrogen in the meta rather than the ortho position relative to the benzene ring of the molecule. The aromatic C=C and C-H functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the C=N group which is also aromatic. The C-C functional group is also equivalent to that of naphthalene. The bonding in isoquinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the C=N group is equivalent to that of pyridine, pyrimidine, pyrazine, and quinoline as given in the corresponding sections.

The symbols of the functional groups of isoquinoline are given in Table 15.315. The corresponding designation of the structure is shown in Figure 73. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of isoquinoline are given in Tables 15.316, 15.317, and 15.318, respectively. The total energy of isoquinoline given in Table 15.319 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.318 corresponding to functional-group composition of the molecule. The bond angle parameters of isoquinoline determined using Eqs. (15.79-15.108) are given in Table 15.320.

Table 15.315. The symbols of functional groups of isoquinoline.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH
$C_b - C_b$ (bridging bond)	C-C
$C_{a,d} = N$	$C \stackrel{3e}{=} N$

Ĕ,	l experimental valu	
<i>C</i> = <i>C</i>	)-0 HD	C=N
Group		
1.47348	1,60061	1.47169
1.31468	1.03299 1.32517	1.27073
1.39140	1.09327 1.40250	1.34489
1.40 (avg.)	1.101 1.42	
(naphthalene)	(benzene) (naphthalene)	ne) (pyridine)
0.66540	1,22265 1.15226	0.74237
0,89223	C9754 U 22780	0.86345

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Bond	Atom	ET	$E_T$	$E_T$	$E_T$	Final Total Energy	runnai /	f, final	$E_{cutof}(C2sp^3)$	$E(C2sp^3)$	. ₀ 3	θ' (9	6, 9	] 'g	<i>d</i> ₁
		(ev) Bond I	(ev) Bond 2	(ev) Bond 3	Bond 4	C2sp ³ (eV)	(a _e )	(a _o )	Final	(eV) Final	E		D	(a ₀ )	(40)
(C-H (C,H)	U"	-0.85035	-0.54343	-0.56690	0	-153,57636	17716.0	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1,22423	0.19124
C-H (C,H)	ů,	-0.85035	-0.54343	-0.56690	0	-153.57636	17716.0	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
(-H (C,H)	ů,	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$N(H)C_4 = C_2$ $N(H)C_3 = C_3$	ບ" ບ້	-0.85035	-0.54343	-0.56690	0	-153,57636	17716.0	0.81052	-16.78642	-16.59556	134.85	45.15	29.72	0.74304	0.57165
$(H)_{C_{k}} = C_{k,k}(H)$	ن	-0.85035	-0.85035	-0.56690	0	-153,88327	17710	0.79597	-17.09334	-16,90248	134,24	45.76	58.98	0.75935	0.55533
$(H)C_{s}(C_{s})C_{s} = C_{s,s}$	ن	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	-16,61903	134.81	45.19	59.66	0.74430	0.57038
$C_{s}(H)C_{s}^{2s} = N$ $C_{s}(H)C_{s}^{2s} = N$	ບີບັ	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50501
$C_{\mu}(H)C_{\mu}^{3a} = N$ $C_{\mu}(H)C_{\mu}^{3a} = N$	×	-0.54343	-0.54343	0	0		0 93084	0,85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
C. (C.)C., -C.	٥٠	-0.85035	-0.85035	-0,28345	0	-153,59983	0.91771	0.80939	-16.80989	-16.61903	95.01	84.99	44.41	1.25451	99020 0

Table 15.318. The energy parameters (eV) of functional groups of isoquinoline.	<ul> <li>V) of functional groups of</li> </ul>	isoquinoline.		
Parameters	C=C Group	C'H Group	C - C Group	C = N Group
J,	0.75	1	1	0.75
$n_{\rm l}$	2	1	1	2
П,	0	0	0	0
n,	0	0	0	0
[5]	5.0	6.75	0.5	0.5
(,,	0.85252	1	1	0,91140
6,		_	1	1
4,	0.85252	17710	0.85252	0,91140
ű	0	1	0	0
6.	3		2	3
2,5	0	-	0	0
. C. j.,	6.5	0.75	0.5	0.5
(2,,	0.85252	1	1	0.91140
V _c (eV)	-101.12679	-37.10024	-34.43791	-102.01431
V, (eV)	20.69825	13.17125	10.26723	21.41410
7' (eV)	34.31559	11,58941	9.80539	34.65890
V,, (eV)	-17.15779	-5.79470	-4.90270	-17.32945
$E(\omega \omega)(eV)$	0	-14.63489	-14.63489	0
ΔΕ _{11,281} (.40 110) (eV)	0	-1.13379	-1.13379	0
$E_T(x_0 m)$ (eV)	0	-13.50110	-13.50110	0
$E_T[u,u\phi]$ (eV)	-63.27075	-31.63539	-31.63529	-63.27076
$E_T(atom - atom, msp^3, AO)$ (eV)	-2.26759	-0.56690	-0.56690	-1.44915
$E_T(\omega)$ (eV)	-65.53833	-32.20226	-32.20226	-64.71988
$\omega \left(10^{15} \operatorname{rad}/s\right)$	49.7272	26.4826	23.6343	43.6311
$E_{\kappa}$ (eV)	32.73133	17.43132	15.55648	28.71875
$\overline{\vec{E}}_D$ (eV)	-0.35806	-0.26130	-0.25127	-0.33540
$\overline{E}_{\text{Kirb}}$ (eV)	0.19649	0.35532 Eq. (13.458)	0.12312   [2]	0.19649
E (eV)	-0.25982	-0.08364	-0.18971	-0.23715
$E_{\rm mag}$ (eV)	0.14803	0.14803	0.14803	0.09457
$E_T(insy)$ (cV)	-49.54347	-32.28590	-32.39198	-48.82472
Eustral (c. 10 HO) (eV)	-14.63489	-14.63489	-14.63489	-14.63489
Emmy (c. 10 110) (eV)	0	-13.59844	0	0
$E_{D}(\mathrm{deap})$ (eV)	5.63881	3.90454	3.12220	4.92005

Table 15.319. The total bond energies of isoquinoline calculated using the functional group composition and the energies of Table 15.318 compared to the experimental values [2]. I.	The David Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of the Constitution of

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				E.	(eV)		-1.83830		ì	-1,85836	
				`.	,		0.79232			0.77426	
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Relative Error	0.00046			ر	5'		_			_	
gy Rela				_	5		_			-	
Experimental Total Bond Energy (eV)	85.44358			,	C2 Atom 2	1	0.79232			0 76801	
				[	C ₂ Atom f		0.79232			0.2080	0.100
Calculated Total Bond Energy	85.4045		$am, msp^3.AO$ .	Atom ?	Hybridization Designation	(Table 15.3B)	88			7-	47
Y II U	Cloup		s Er (atom - al		Econtombic Atom 2		-17.17218			273.00	-17,71560
U-C	ding 15		tal values [1]. Er i		Atom I Hybridization Designation	(Table 15.3B)	30	2			21
H.)		,	id experimen		E. Gostombie Atom I	_	פוניניניו	2.62936   2.65034   4.5565   -17.17210			-17 43216
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energies of			a narameter	c parameter	2c' Band I	Ì		2.62936			SISE A CALLS C PLILLS
Table 15.319. The total bond energies of isoquinomic caronatas transfer to the forms $C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C_{-1}^{-1}C$		C ₃ H ₂ N Isoquinoline	$\pi$ 1. If $\pi$ 2. The band and a remarkers of isominoline and experimental values [1], $E_{\tau}$ is $E_{\tau}(atom-atom, my^2,AO)$ .	Table 13,320. The point angi-	Alanys af Angle			70.00		H:),)7	

### **INDOLE**

Indole having the formula  $C_8H_7N$  comprises a phenyl moiety with a conjugated five-membered ring which comprises pyrrole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure. 74. The aromatic  $C_-^{3e}C$  and C-H functional groups of the phenyl moiety are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section. The CH, NH, and  $C_d = C_e$  groups of the pyrrole-type ring are equivalent to the corresponding groups of pyrrole, furan, and thiophene where present as given in the corresponding sections. The  $C_b - C_d$  single bond of aryl carbon to the  $C_d = C_e$  bond is also a functional group. This group is equivalent to the C - C(O) group of benzoic acids with regard to  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) both being -1.29147~eV. This energy is a linear combination of  $\frac{-1.13379~eV}{2}$ ,  $E_T(atom-atom,msp^3.AO)$  of the C-H group that the  $C_b - C_d$  and C - C(O) groups replace, and that of an independent  $C2sp^3$  HO, -0.72457~eV (Eq. (14.151)). However, as in the case of pyrrole, the indole hybridization term  $c_2$  is the aromatic  $c_2(benzeneC2sp^3HO) = 0.85252$  to match the aryl  $C2sp^3$  HO, and the energy terms corresponding to oscillation in the transition state correspond to indole.

As in the case of pyrrole, the C-N-C-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1=2$  in Eqs. (15.42) and (15.52). The hybridization factor  $c_2(arylC2sp^3HO\ to\ N)=0.84665$  (Eq. 20 (15.152)) matches the aromatic character of the  $C2sp^3$  HOs to the N atom of the NH group, and  $C_2$  and  $C_{2o}$  in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143),  $C_2(benzeneC2sp^3HO)=0.85252$ . Furthermore,  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) are both  $-2.42526\ eV$  which is a linear combination of  $\frac{-1.13379\ eV}{2}$ ,  $E_T(atom-atom,msp^3.AO)$  of the C-H group that the 25  $C_c-N$  bond replaces, and  $-1.85836\ eV$  (Eq. (14.513)) which is equivalent to the corresponding component of the C-N-C-bond of pyrrole.

The symbols of the functional groups of indole are given in Table 15.321. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of indole are given in Tables 15.322, 15.323, and 15.324, respectively. The total energy of indole given in Table 15.325 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.324 corresponding to functional-group composition of the molecule. The bond angle parameters of indole determined using Eqs. (15.79-15.108) are given in Table 15.326.

Table 15.321. The symbols of functional groups of indole.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH (i)
$C_d = C_e$ double bond	C = C
$C_b - C_d$	C-C
CH	CH (ii)
$C_c - N - C_e$	C-N-C
NH group	NH

					•			
	NH	Group	1.24428	0.94134	0.996270	0.996 (pyrrole)	0.81370	0.75653
	C-N-C	Group	1.44394	1.30144	1.37738	1.370 (рулоlе)	0.62548	0.90131
	2-2	Group	1.81395	1.34683	1.42542	1,417 (pyrrole)	1.21510	0.74248
	(H (ii)	Group	1.53380	1.01120	1.07021	1.076 (pyrrole	1.15326	0,65928
mnental values [1].	<b>C</b> ≈C	Group	1.45103	1.30463	1.38076	1.382 (pyrrole)	0.63517	0.89910
parameters of indole and experimental values [1]	() H.)	Group	19009'1	1.03299	1.09327	1.101 (benzene)	1,22265	0.64537
he geometrical bond param	ر ار در	Group	1.47348	1.31468	1.39140	1.399 (benzene)	0.66540	0.89223
l able 15.522. I h	,	Parameter	a (a ₀ )	c' (a _o )	Bond Length $2c'(A)$	Exp. Bond Length (A)	$b,c$ $(a_o)$	в

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Table 15.323. The M		
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$\begin{pmatrix} d_1 \\ (a_0) \end{pmatrix}$	0.21379	0.55533	0.55124	0.55328	0.02914	0.00729	0.60208	0.60425	0.61064	0.64061	0.41796	0.58048
$a'_i$ $(a_o)$	1,24678	0.75935	0.76344	0.76140	1.37597	1,33953	0.70255	0.70038	0.69080	0.66083	0.52338	0.72095
(°)	38.84	58.98	58.79	58.89	40.66	42.40	61.04	61.14	61.42	62.76	65.13	60.05
θ, (°)	105.58	45.76	45.91	45.84	92.11	89.49	42.71	42.63	41.97	40.96	60.48	43.03
(₀) ,θ	74.42	134.24	134.09	134.16	87.89	90.51	137.29	137.37	138.03	139.04	119.52	136.97
$E(C2xp^3)$ (eV) Final	-16.90248	-16.90248	-16,98132	-16.94190	-16,98132	-16.41442	-16,41442	-16.37500	-16.37500			-16.94189
(eV) Final	-17.09334	-17.09334	-17.17218	-17.13276	-17.17218	-16,60528	-16.60528	-16.56586	-16.56586	-16.03838	-16.03838	-17.13276
$\binom{f_{(m,n)}}{a_0}$	0.79597	0.79597	0.79232	0.79414	0.79232	0.81937	0.81937	0.82132	0.82132	0.84833	0.84833	0.79414
(op)	17716.0	17716.0	0.91771	0.91771	17716.0	17716,0	17716.0	17716.0	0.91771	0.93084	0.93084	0.91771
Final Total Energy (72sp³ (eV)	-153.88327	-153.88327	-153.96212	-153,92270	-153.96212	-153.39522	-153,39522	-153.35580	-153.35580			-153.92269
E _T (eV) Bond 4	0	0	0	0	0	0	0	0	0	0	0	0
E _r (eV) Bond 3	-0.56690	-0.56690	-0.85035	-0.85035	-0.64574	0	0	0	0	, 0	0	-0.60631
E _T (eV) Bond 2	-0.85035	-0 85035	-0.64574	-0.85035	-0.85035	-(.13379	-1.13379	-0,60631	-0.60631	-0.60631	-0.60631	-0.85035
(eV) Bond I	-0.85035	-0.85035	-0.85035	-0.60631	-0.85035	-0.64574	-0,64574	-1.13379	-1.13379	-0.60631	-0.60631	-0.85035
Atom	ئن ا	ో	ن	ີ່	ڻ	2	6.7	ڻ	ٹن ٔ	2	N	ن
рио	-H (C,H)	34 36 = H("=(")25	$\sum_{j=1}^{N_{p}} (x_{j}^{j})(x_{j}^{j} = 0, x_{j}^{j})$ $\sum_{j=1}^{N_{p}} (x_{j}^{j})(x_{j}^{j} = 0, x_{j}^{j})$	"=C; (N)C; "=C; (N)C;	(H)C, -C,(H)C,	(H)C, -C,(H)C,	$(H)C_{r}=C_{r}N$	$(H)C_d = C_s N$	JC - NC.	,C, – MC,	- H (NH)	C - NC

Table 15.324. The energy parameters (eV) of functional groups of indole	rs (ev) or runcuon	al groups of moore	,				
Parameters	C=C Group	CH (i) Group	C = C Group	C-C Group	CH (ii) Group	C-N-C Group	WH Group
- J	0.75	1	1	1	1	1	1
П,	2		2	1	1	2	
n,	0	0	0	0	0	0	0
n,	0	0	0	0	0	0	0
C,	0.5	0.75	0.5	5.0	0.75	0.5	0.75
(,	0.85252	-	0.85252	_	1	0.85252	0.93613
6,	-	-		1	1	1	0.75
6,	0.85252	0.91771	0.85252	0.85252	17716.0	0.84665	0.92171
5	0	-	0	0	1	0	1
ยั	3	-	4	2	1	4	1
ŭ	0	-	0	0	1	0	1
	0.5	0.75	0.5	0.5	0.75	0.5	0.75
C ₂ ,	0.85252	-	0.85252	1	1	0.85252	1
V, (eV)	-101.12679	-37.10024	-104.37986	-32,93291	-39.09538	-104.73877	-39.48897
V, (eV)	20.69825	13.17125	20.85777	10.10210	13,45505	20.90891	14.45367
T (eV)	34,31559	11.58941	35.96751	9.07768	12.74462	36.26840	15.86820
V (eV)	-17.15779	-5.79470	92886'21-	-4.53884	-6.37231	-18.13420	-7.93410
E(so no) (eV)	0	-14.63489	0	-14.63489	-14.63489	0	-14.53414
$\Delta E_{\mu, 1, m}(so m)$ (eV)	0	-1.13379	-2,26759	-1.29147	-2.26758	-2.42526	0
E_(.v m) (eV)	0	-13.50110	2.26759	-13.34342	-12.36731	2.42526	-14.53414
$E_{\tau}(u_1,u_2)$ (cV)	-63.27075	-31.63539	-63.27075	-31.63539	-31,63533	-63.27040	-31,63534
$E_{\tau}(atom - atom, mxp^3, AO)$ (cV)	-2,26759	06995.0-	-2,26759	-1,29147	0	-2.42526	0
$E_r(in)$ (aV)	-65,53833	-32.20226	-65,53833	-32.92684	-31.63537	-65,69600	-31.63537
ω (10 ¹⁵ rad / s)	49.7272	26.4826	15.4421	21.8249	28.9084	54,5632	48.7771
$E_{K}$ (eV)	32.73133	17.43132	10.16428	14,36554	19.02803	35.91442	32.10594
$\overline{E}_{D}$ (eV)	-0.35806	-0.26130	-0.20668	-0.24690	-0.27301	-0.38945	-0.35462
$\overline{E}_{\mathrm{Kish}}$ (eV)	0.19649	0.35532 Eq. (13.458)	0.17897 [6]	0.12312 121	0.39427	0.11159 [12]	0.40696
<u>E</u> (eV)	-0.25982	-0.08364	-0.11720	-0.18534	-0.07587	-0.33365	-0.15115
$E_{m_{N}}\left( eV ight)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{T}(inup)$ (cV)	-49.54347	-32,28590	-65.77272	-33.11218	-31.71124	-66,36330	-31.78651
E (c10 110) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,53414
E 110 (c. 10 10) (eV)	0	-13.59844	0	0	-13,59844	0	-13.59844
$E_{\rm p}(\epsilon_{\rm inup})$ (eV)	5.63881	3.90454	7.23317	3.84240	3.32988	7.82374	3.51208
	•						

Table 15.325. The total bond energies of indole calculated using the functional group composition and the energies of Table 15.324 compared to the experimental values [2].  Formula Name $C_{=C}^{3r}$ $CH$ (i) $C = C$ $C + C$ (ii) $C - N - C$ $NH$ Total Bond Energy Total Bond Energy Relative Energy Total Bond Energy (eV)		Tor	
lated using the functional group composition and the energies of Table 15.324 compared to the experimental values [2]. $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$ $C = C$		Relative Error	
lated using the functional group composition and the energies of Table 15.324 compared to the experime $C = C \qquad C + C \qquad CH \ (ii) \qquad C - N - C \qquad NH \qquad Total C + C \qquad CH \ (ii) \qquad C - N - C \qquad CH \ (ii) \qquad C - N - C \qquad CH \ (ii) \qquad C - N - C \qquad CH \ (iii) \qquad C - N - C \qquad CH \ (iiii) \qquad C - N - C \qquad CH \ (iiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiii$		Experimental Total Bond Energy	(ev)
lated using the functional group composition and the energies of Table 15.7 $C+C$ $CH$ (ii) $C-C$	xperimental values [2]	Calculated Total Bond Energy	(64)
lated using the functional group composition and the energies of Table 15.7 $C+C$ $CH$ (ii) $C-C$	red to the e	NH	
lated using the functional group composition and the ene $C + C + C + C + C + C + C + C + C + C $	ible 15.324 compa		
lated using the functional group composition $C = C$	energies of Ta	CH (ii)	
lated using the functional g	position and the	2-2	
Table 15.325. The total bond energies of indole calculated using the function Formula Name $C = C + (H \ (i) + C.H.N$	nal group com	<i>C</i> = <i>C</i>	
Table 15.325. The total bond energies of inclole calculated Formula Name $C = C$	using the function	(J) H.)	,
Table 15.325. The total bond energies of Pormula Name	indole calculated	C = C	7
Formula	he total bond energies of i	Name	dole
	Table 15,325. TI	Formula	C.H.N

			Exp. <i>\theta</i>		[20-23] 021	(benzene)	120 [50-52]
			(°)		120 19		16.611
			(°)				
			θ ₋ (O)				120.19
	,	1	r (0)				
	-0.00010	9).	E _T (eV)		-1.85836		
e ?	78.514	atom, msp³.A(	20"		0.79232		
		(atom – t	ď.		-		
(eV)	78.52215	L E, is E,	5		-		
		e were used	υ	-	-		
	_	ceding angle	C ₂ Atom 2		0.79232		
		rom the pre	C ₂		0.79232		-
	2	$s$ [1]. In the calculation of $\theta_s$ , the parameters from the preceding angle were used. $E_r$ is $E_r$ (anom – anom, msp ² , AO).	Atom 2 Hybridization Designation	(TOTAL STATE	20		
	-	culation of 6	EContombre Atom 2		-17.17218		
	-	dues [1]. In the cal	Atom I Hybridization Designation	T	20		
	4	erimental va	Ecasbarke Atom 1		-17.17218		
,	٥	e and exp	2c' 1cmiiul Atoms (a ₀ )		4.5585		
		s of indol	2c' Bond 2 (a ₀ )		2.62936		
		e parameter.	2c' Bond I (a _n )		2.62936 2.62936 4.5585 -17.17218		
N.H.		Table 15.326. The bond angle parameters of indole and experimental values	Atoms of Angle	CCCC	(aromatic)	HC:CH	(aromatic)
2		Ta					

#### **ADENINE**

20

Adenine having the formula  $C_5H_5N_5$  comprises a pyrimidine moiety with an aniline group and a conjugated five-membered ring which comprises imidazole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure. 75. The aromatic C = C, C - H, and C = N functional groups of the pyrimidine moiety are equivalent to those of pyrimidine as given in the corresponding section. The  $NH_2$  and  $C_a - N_a$  functional groups of the aniline moiety are equivalent to those of aniline as given in the corresponding section. The CH, NH,  $C_d - N_e$ , and  $N_e = C_e$  groups of the imidazole-type ring are equivalent to the corresponding groups of imidazole as given in the corresponding section. The C-N-C functional group of the imidazole-type ring is equivalent to the corresponding group of indole having the same structure with the C-N-C group bonding to aryl and alkenyl groups.

The symbols of the functional groups of adenine are given in Table 15.327. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of adenine are given in Tables 15.328, 15.329, and 15.330, respectively. The total energy of adenine given in Table 15.332 was calculated as the sum over the integer multiple of each  $E_D(G_{POMP})$  of Table 15.330 corresponding to functional-group composition of the molecule. The bond angle parameters of adenine determined using Eqs. (15.79-15.108) are given in Table 15.332.

Table 15.327. The symbols of functional groups of adenine.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH (i)
$C_{b,c} \stackrel{3e}{=} N_c \qquad C_{a,b} \stackrel{3e}{=} N_b$	$C \stackrel{3e}{=} N$
$C_a - N_a$	C-N (a)
NH ₂ group	$NH_2$
$N_e = C_e$ double bond	N = C
$C_d - N_e$	C-N (b)
$N_dH$ group	NH
CH	CH (ii)
$C_c - N_d - C_e$	C-N-C

Table 15.328. The geometrical bond parameters of adenne and experimental values [1]	metrical bond paramete	ers of adenu	ne and experime	ntal values											-	
Parameter	ر <del>ا</del> ر		CH (i) Group	C=N Group		C-N (a) Group	NH ₁ Group		N = C Group	ن -	C-N (b) Group	NH Group		CH (II) Group	20	Group
a (a _o )	1,47348	-	1,60061	1.47169	-	1.81158	1.24428		1.44926	1.	1.82450	1,24428	8	1.53380	1,	1.44394
c' (a ₀ )	1,31468	<u> </u>	1.03299	1,27073		1.34595	0.94134		1.30383	1.	1,35074	0,94134	-	1.01120	1	1.30144
Bond Length 2c' (A)	1.39140	ند	1.09327	1.34489		1.42449	0.99627		1.37991	1.	1.42956	0.996270	0.	1.07021		1.37738
Exp. Bond Length	1.393 (pyrimidine)	<u>.</u>	1.084 (pyridíne)	1,340 (pyrimidine)		1.431 (aniline)	0,998 (aniline)					0.996 (pyrrole)	3)	1.076 (pyrrole)		1.370 (pyrrole)
h,c (a,)	0.66540	_	1,22265	0.74237		1.21254	0.81370		0.63276	-	1.22650	0.81370		1.15326	o L	0.62548
c ( 0)	0.89223	Ö	0.64537	0.86345		0.74297	0.75653		0.89965	0	0.74033	0,75653	3	0.65928	0.	0.90131
Table 15.329. The MO to HO intercept geometrical bond parameters	to HO intercept geom	etrical bond	l parameters of a	denine. R _i is a	n alkyt group an	d R,R',R" are	of adenine. $R_i$ is an alkyl group and $R_iR_i^*R^*$ are $H$ or alkyl groups.		$E_{\tau}$ is $E_{\tau}(alom-alom,msp^{3}.AO)$	nsp³.AO].	į					
Bond		Atom	E _r (eV) Bond 1	E _T (eV) Bond 2	E _r (eV) Bond 3	$E_{\tau}$ (eV) Bond 4	Final Total Energy C2sp³	$(a_o)$	$(a_0)$	Econo (C2sp²) (eV) Final	$E(C2sp^3)$ (eV) Final	. (C)	· (C)	(°)	(a,)	$(a_o)$
$C_s(N_b)C_sN_sH-H$		χ'	-0.56690	0	٥	0		0.93084	0.88392	-15.39265		121.74	58,26	67.49	0.47634	0.46500
$C_s(N_s)C_s - N_sH_2$		ڻن	-0,56690	-0,54343	-0.85035	0	-153,57636	177160	0.81052	-16.78642	-16.59556	89.90	90.10	41.95	134737	0,00142
$C_J(N_b)C_s-N_aH_2$		≥,	-0.56690	5	0	0		0.93084	0.88392	-15.39265		96.32	83.68	46.43	1.24859	0 09736
$C-H(C_sH)$		ڻ	-0.54343	-0.54343	-0.36690	0	-153,26945	17716.0	0.82562	-16.47951	-16,28864	78.27	101.73	4139	1,20084	0,16785
C-H (C,H)		ن.	4(92918	-0.60631	D	0	-153,15119	12216.0	0.83159	-16,36125	-16.17038	79.01	66'001	41.89	1.19159	0.15860
$(H_xN)H-N$		×	-0.60631	-0,60631	0	0		0,93084	0,84833	-16.03838		119.52	60,48	65.13	0.52338	0.41796
$C_a(NH_1)C_a = N_aC_a$		٠,٠	-0,85035	-0,54343	-0.56690	0	-153,57636	177160	0.81052	-16.78642	-16.39556	128.54	51.46	58.65	0.76572	0.50501
$C_d(NH_2)C_a=N_bC_b$ $N_cC_a=N_cC_a$		x x	-0.54343	-0,54343	0	o		0.93084	0.85503	-15.91261		130.61	49.39	50.97	0,71418	0,55656
N,C,=N,C, N,C,=N,C,		<b>ೆ</b>	-0.54343	-0.54343	-6.56690	e	-153,26945	17716.0	0.82562	-16.47951	-16.28865	92 671	50.74	59.44	0 74824	0,52249
$C_{\sigma}(N_{\sigma}H)C_{\sigma}=N_{\sigma}C_{\sigma}$		ئ	-0,85035	-0,54343	15000.0-	5	-153,61578	17116.0	0,80%63	-16.82584	-16.63498	128.45	51.55	58.53	0.76792	0,50281
$N_{\delta}(N_{\sigma}H_{2})C_{\sigma} = C_{\sigma}(N_{\sigma})C_{\sigma}$	)ز:	5,	-0.85035	-0.54343	-0.56690	0	-153,57636	17716.0	0.81052	-16.78642	-16.39556	134,85	45.15	59.72	0.74304	0,57165
$N_{\delta}(N_{\sigma}H_{2})C_{\sigma} = C_{\sigma}(N_{\sigma})C_{\sigma}$ $C_{\sigma}(N_{\sigma})C_{\sigma} = C_{\sigma}(N_{\sigma}H)N_{\sigma}$	)c, N,	Č,	-0,85035	-11,85035	65474.0-	8	-153.7K/97	17710.0	0.80076	-16.99103	-16.80017	134,41	45.56	59.22	0.75398	12095.0
$C_{\alpha}(N_{\alpha})C_{\alpha}=C_{\alpha}(N_{\alpha}H)N$	, N	٤٠	-0,85035	-0.54343	-0.60631	Þ	-153,61578	0.91771	0.80863	-16.82584	-16.63498	134.77	45.23	29.62	0,74516	0.56952
C, (N,)C, -N,H		٠,٠	-0.85035	-0.54343	-0,66631	0	-153,61578	17710.0	0,80863	-16.82584	-16.63498	H5.761	42.46	80.78	0,70488	0.59656
$C_s(H)N_s - C_s(N_s)C_s$ $N_s(H)C_s - N_s(H)C_s$		Ν,	-0,6063 [	-0,68631	ij.	a		0.93084	0.84833	-16.03838		139.04	+0.96	62.76	0,66083	0,64061
$N_r(H)C_r - N_s(H)C_r$		Ü	-11,60631	*1929.0	0	0	-153.15119	0.91771	0,83159	-16.36125	-16.17039	138.42	41.58	61.93	0,67940	0,62203
$C_dN_s = C_s(H)N_sH$			-0,92918	16909,0-	D	0	-153,15119	122160	0.83159	-16.36125	-16,17039	137,93	42.07	61.72	0.68657	0.61726
$C_{a}N_{c}=C_{c}(H)N_{d}H$		ν,	-0 92918	-0.46459	0	0		0,93084	0.83885	-16.21952		138,20	41.80	62.03	0.67849	0.62534
(こ)(こ)( ール) こ		'n	-0,46459	-0.92918	0	0		0 93084	0,83885	-16.21952		91.32	89'88	43.14	133135	0.01939
'. (. ') c. ' - N 'c.'		ن	-0,46459	-0.85035	-0,85035	0	-153,78097	17710,0	0.80076	-16.99103	-16.80017	87.71	92.29	40.72	1.38280	0,03206

	ł	1	,			-				
Parameters	U = C	CH (3) Group	C=N Groun	C~N (a) Group	NH, Group	N=C Group	C-N (b) Group	Group	CH (ii) Group	C-N-C Group
	0.75	-	0.75	_	-	-		ı	I	1
	-	-	7	-	2	2	-	-	-	2
	4 6			0	0	0	0	0	0	0
				0		0	0	0	0	0
	200	0.75	90	0.5	0.75	0.5	0.5	0.75	0.75	0,5
	0.85757	-	0.91140		0.93613	0.85252		0,93613	1	0.85252
-	1		-		0.75	I	-	0.75	-	-
	0.85252	17710	0.91140	0.84665	0.92171	0.84665	0.84665	0.92171	0.91771	0.84665
6,	0	-	0	0	0	0	0	1	1	0
	3	-	3	2	-	4	2	1	1	4
	0	-	0	0	2	0	0	1	-	0
	0.5	0.75	0.5	6.5	1.5	0.5	0.5	0.75	0.75	0.5
	0.85252	-	0.91140		1	0.85252	1	1	1	0.85252
V, (eV)	-101,12679	-37.10024	-102.01431	-32.76465	-78.97795	-103.92756	-32,44864	-39.48897	-39.09538	-104.73877
V, (eV)	20.69825	13,17125	21.41410	10.10870	28.90735	20.87050	10.07285	14.45367	13.45505	20.90891
T (eV)	34.31559	11.58941	34.65890	9,04312	31.73641	35.85539	8.89248	15.86820	12,74462	36.26840
V_ (eV)	-17.15779	-5.79470	-17.32945	-4.52156	-15.86820	-17.92770	-4.44624	-7.93410	-6.37231	-18.13420
E(10 110) (eV)	0	-14.63489	0	-14.63489	-14.53414	0 .	-14.63489	-14.53414	-14.63489	0
DE LA HO (AO HO) (eV)	0	-1.13379	0	-1.13379	0	-1.85836	0.92918	0	-2.26758	-2.42526
E. (30 10) (eV)	0	-13,50110	0	-13.50110	-14,53414	1.85836	-13.70571	-14,53414	-12.36731	2.42526
E(n, 10 110] (eV)	0	0	0	0	-14,53414	0	0	0	0	0
E. (u,10) (eV)	-63.27075	-31.63539	-63.27076	-31,63549	-48.73654	-63.27100	-31.63527	-31.63534	-31.63533	-63.27040
$E_T(atom - atom, msp^3, AO)$ (eV)	-2.26759	-0.56690	-1.44915	-1.13379	0	-1.85836	-0.92918	0	0	-2.42526
E. [110] (eV)	-65.53833	-32,20226	-64.71988	-32.76916	-48.73660	-65.12910	-32,56455	-31.63537	-31.63537	-65.69600
ω (101* rad / s)	49.7272	26.4826	43,6311	0686'11	68.9812	15,4704	21,5213	48.7771	28.9084	54.5632
E. (eV)	32.73133	17.43132	28.71875	7.89138	45.40465	10.18290	14.16571	32,10594	19.02803	35.91442
$\overline{\vec{E}}_n$ (eV)	-0.35806	-0.26130	-0.33540	-0.18211	-0.42172	-0.20558	-0.24248	-0.35462	-0,27301	-0.38945
$\overline{E}_{kmb}$ (eV)	0.19649	0.35532 Eq. (13.458)	0.19649	0.15498 [54]	0.40929 [22]	0,20768	0.12944 [23]	0.40696 [24]	0.39427 [56]	0.11159
E (cV)	-0.25982	-0.08364	-0,23715	-0.10462	-0.21708	-0.10174	-0.17775	-0.15115	-0,07587	-0.33365
$E_{mg}$ (eV)	0.14803	0.14803	0.09457	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Er Grangel (eV)	-49.54347	-32,28590	-48.82472	-32,87379	-49.17075	-65.33259	-32.74230	-31,78651	-31.71124	-66.36330
E 10 110] (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14,53414	-14.63489	-14.63489	-14,53414	-14.63489	-14.63489
Emiser (c. 10 110) (eV)	0	-13.59844	0	0	-13.59844	0	0	-13.59844	-13.59844	
E. Cirran (eV)	5.63881	3.90454	4.92005	3.60401	7.43973	6.79303	3.47253	3.51208	3,32988	7.82374

Table 15.331. The total bond energies of adeninc calculated using the functional group composition and the energies of Table 15.330 compared to the experimental Values (2).  Calculated Experimental Values (2).  Calculated Experimental Values (2).  Calculated Experimental Values (2).  Calculated Experimental Values (3).  Calculated Experimental Values (4): $C = N$ (4): $N = C = N$ (5): $N = C = N$ (6): $N = C = N$ (7): $N = C = N$ (7): $N = C = N$ (7): $N = C = N$ (7): $N = C = N$ (7): $N = C = N$ (7): $N = C = N$ (7): $N = C = N$ (7): $N = C = N$ (7): $N = C = N$ (7): $N = C = N$ (7): $N = C = N$ (7): $N = C = N$ (8): $N = C = N$ (9): $N = C = N$ (7): $N = C = N$ (7): $N = C = N$ (7): $N = C = N$ (8): $N = C = N$ (9): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C = N$ (1): $N = C =$
the functional group composition and the energies of Table 15,330 compared to the experimental values [2]. Calculated (i) $C=N$ (a) $MH_1$ $N=C$ $C-N$ (b) $NH$ $CH$ (ii) $C=N-C$ Total Soral Bond Bond Energy Choup Group $G$ and $G$ $G$ $G$ $G$ $G$ $G$ $G$ $G$ $G$ $G$
the functional group composition and the energies of Table 15.339 compared to the experimental values $ J_{\perp} $ .  (i) $C=N$ (ii) $M_{\perp}$ $N=C$ $C-N$ (b) $NH$ $CH$ (ii) $C-N$ (c) $C+N$ (c) $C+N$ (c) $C+N$ (d) $C+N$ (d) $C+N$ (d) $C+N$ (e) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (f) $C+N$ (
the functional group composition and the energies of Table 15.530 compared to the experimental values $I$ (i) $C=N$ (a) $NH_1$ , $N=C$ $C-N$ (b) $NH$ $I$ $I$ $I$ $I$ $I$ $I$ $I$ $I$ $I$ $I$
the functional group composition and the energies of Table 15,350 compared to the experiment $(i)  C=N  C-N  (a)  NH; \qquad N=C  C-N  (b)  NI$ $(i)  Group  Group  Group  I  I  I  I  I  I  I  I  I  $
the functional group composition and the energies of Table 15,330 compare $(i)$ $C=N$ $C=N$ (a) $NH$ , $N=C$ $C$ $C$ Group Group Group $I$ $I$ $I$ $I$ $I$ $I$ $I$
the functional group composition and the energies of Lable 1 (i) $C=N$ (a) $NH_1$ , $I$ (f) $G=N$ (Group Group 1 1 1
the functional group composition and the end $f(i) = \begin{pmatrix} C = N & C - N & (a) \\ Group & Group \end{pmatrix}$
the functional group composition at $f(i)$ $C = N$ $C - N$ ( Group Group $G$
(i)
Table 15.331. The total bond energies of adehine calculated using the time. Formula Naive $C = C$ (7 $H$ (f) CAHA.
Table 15.331. The total bond energies of adenino calcula. Formula Name $C = C$ CARAN. Advanta 2
Table 15.331, The total bond energies Formula Name C.H.M.
Fomula Formula Ad

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$\exp \theta$	113.9 [1] (aniline)	811	115	126	611	127	114.4	1,27.8	128.9	1.9.7	110.4	105.9	126.4	118.2	122.1	132.8	103.3	106.1	uli3	118.6	116.7
Cal. 9 (9)	113.89	123 60	117.65	122.35	125.02	128.35	112.64	128.11	128.73	122.22	110.56	106.60	119.73	119.73	76.711	133,55	106,93	110.07	118.09	118,59	116.52
(e)					112.64																
(9)					122.35																
φ (o)																					
E _T (eV)	0	D	Û	0		0	-1.44915	-1.44915	-1.44915	-1.44915	-1,44915	-1.44915	-1.44915	-1.44915	-1.44915	-1,44915	-1.85836	-1.85836	-1.85836	-1,85836	-1.85836
'ئ'	1.06823	1,01912	0.99312	1.01811		1.10912	0,84359	0.87902	0.87495	0.86947	0.84958	0.82371	0.85608	0.85608	0.86734	0.91456	0.75924	0.76631	0.77393	0.77478	0.78071
· '5	0.75	0.75	0.75	0.75		0.75		-,	Ī	-	/ <b>-</b> -		1	-	1	-	-	_		_	-
5	-		1	-		-	1		1	-		1	1	ī		_	1	1	-	×	-
כל	-	0.75	0.75	0.75		0.75				-	-		-	1	_	-	1	-	-		-
C ₂ Atom 3	-	0.86284 (Eq. (15.64))	0.91140 Eq. (15.116))	0.84665 Eq. (15.152))		0.86284 (Eq. (15.64))	0.84833	0.84665 Eq. (15.152))	0.87495	0.88392	0.85252	0.80076	920030	0.80076	0.82327	17716.0	0.75924	0.76631	0,76631	0.78155	0.79340
C ₂	0.93613 Eq. (13.248))	0.84665 (Eq. (15.152))	0.91771	0.83159		0.84665 (Eq. (15.152))	0.83885	0.91140 Eq. (15.116))	0.87495	0.85503	0.84665 (Eq. (15.152))	0,84665 (Eq. (15.152))	0,91140 Eq. (15,116))	0.91140 Eq. (15.116))	0.91140 Eq. (15.116))	0.91140 Eq. (15.116))	0.75924	0.76631	0,78155	0.76801	0.76801
Atom 2 Hybridization Designation (Table 15.3B)	Ξ	v	N	z		٠,	7	z	3	2	۷	91	16	91	12	-	28	25	25	21	19
E centonibe Atom 2	I	-15,95955	-14,53414	-[4,534]4		-15.95955	-16.03838	-14.53414	-15,55033	-15.39265	-15.93935 C _c	-16.39103 C _a	-16.99103 C _d	-16.99103 C _d	-16.52644 C ₃	-14.82575 C_	-17.92022	-17,75502	-17,75502	-17,40869	-17,14871
Atom 1 Hybridization Designation (Table 15.3B)	z	z	_	QI.		z	8	z	3	ç	Z	. 2	z	z	z	z	28	25	12.	24	24
E Contombre Atom 1	-14,53414	-14.53414	-14.82575	-16.36125		-14.53414	-16.21952	-14.53414	-15.55033	-15.91261	-14.53414	-14.53414	-14.53414	-14.53414	-14.53414	-14.53414	-17.92022	-17.75502	-17.40869	-17.71560	-17.71560
2c' Terminal Atoms (a ₀ )	3.1559	4,0497	3.9497	4.0561		4,0497	4,3359	4.6260	4.5826	4.5826	4.3818	4.1952	4.4721	4.4721	4.5607	4.8990	4.2661	4.2661	4.3589	4.3704	4.4721
2c' Bend 2 (a ₀ )	1.88268	2.69190	2.54147	2.60766	-	2.60287	2.60287	2.60287	2.54147	2.69190	2,62936	2.62936	2.62936	2.62936	2.62936	2.62936	2.60766	2.60287	2.54147	2.54147	2.62936
2c'	1.88268	1 88268 2	2,06598	2,02241		1,88268	2.60766	2.54147	2,54147	2.54147	2.70148	2,60287	2.54147	2,54147	2.69190	2,70148	2,70148	2.60287	2.54147	2,54147	2,62936
Alonis of Angle	HNH7	ZHW."	ZH,C,N, ZH,C,N,	ZH,C,N,	ZH,C,N,	2H,N,C, 2H,N,C,	ZN,C,N,	, ZN,C.,N _d	ZN,C,N,	ZN,C,N,	ZN,C,C.	ZNJC,C,	ZN,C,C,	ZN,C,C,	כא'כ"כ"	ZN,C,C,	7C,N,C,	, N, V, J.	ZC,N,C,	ZC,N,C,	້ວໃນ"OZ

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While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.

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